Defluoridation of water using neem (Azardiracta Indica) leaf powder (NLP)

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Abstract

In this study, dry powder of bioadsorbent was prepared from neem tree leaves by crushing the dry leaves and the prepared powder of bioadsorbent was used to remove fluoride from aqueous solutions. The produced bioadsorbent was characterized by measuring their porosities and pore size distributions. The microstructure of the bioadsorbent was examined by scanning electron microscopy (SEM). The resulting activated bioadsorbent was used for removal of fluoride from aqueous solution. The effects of pH, temperature and contact time were investigated. Isotherm studies were carried out and the data were analyzed by Langmuir and Freundlich equations. Two simplified kinetic models were tested to investigate the adsorption mechanism.

Keywords: Bio-Adsorbent, Adsorption, Fluoride, Chemical activation.

Introduction

Presence of Fluoride in drinking water can be harmful (Dobaradaran *et al.,*2008; Dobaradaran *et al.,*2008) and the WHO have given the upper acceptable level of F in drinking water as 1–1.5 mg/L (Veeraputhiran & Alagumuthu, 2010). As concentrations above this range can lead to adverse effects on human health (Alagumuthu & Rajan, 2008; Jamode *et al.,* 2004; Miramontes *et al.,*2003; Mondal *et al.,* 2013). Fluoride has been considered as both an essential element and potent environmental pollutant at high concentrations causing fluorosis among the consumers. Fluorosis in general, has been identifies in various countries. In India, most of the water bodies are highly contaminated by fluoride with varying concentration in the range of 0.5-20 mg/L (Srimurali *et al.,* 1998*;* Mahvi *et al.,* 2006). Excessive presence of

fluoride (F) in potable water continues to be a serious public health concern in many parts of the world, including India.

The removal of Fluoride from high Fluoride water is necessary to make it safe for drinking and cooking. Various techniques have been used for F removal such as adsorption on activated alumina, alum, ferric hydroxide, ash, and ion exchange resins; membrane processes such as nanofiltration, reverse osmosis and electro dialysis; and chemical precipitation (Shams *et al.,* 2010; Telesiński *et al., 2011;* Alagumuthu *et al.,* 2011*;* Arulanantham *et al.,*1992; Kumar *et al., 2007*). Among these, adsorption has shown considerable potential in defluoridation of wastewater. Within last few years, the plant based bioremediation approach to improve the quality of water has become an area of intense study. (*Carbon*, 2004; Venkata Naga Baji Tokala and Pankaj Guptha, 2014) various plant materials like coconut shell (Arulanantham *et al.,* 1992), bone char, (Kumar *et al.,* 2007) tamarind seed, neem and kikar leaves (G. Alagumuthu *et al*. 2010), Barmuda grass (Chakrabarty and Sarma, 2012), neem charcoal (Gisele *et al.,* 2012),Moringa oleifera seed (American Public Health Association, 2007) have also been used as adsorbents for defluoridation. Activated carbon is widely used in water treatment. Bioremediation is recognized as a cost-effective and environmental friendly option for cleanup of contaminated water. The present study has been carried out to investigate the performance and efficiency of activated stalks of sorghum and canola for F adsorption from water under laboratory conditions.

Materials and Methods

All the reagents used were of AR grade. Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in 1000 ml distilled water in volumetric flask. Fluoride standard solution was prepared by diluting 100 ml stock solution to 1000 ml distilled water in volumetric flask. This 1 ml solution has 0.1 mg of fluoride.

Equipment

The amount of fluoride ions was measured by pH ion meter 363 with ion selective electrode as per standard methods. pH meter (systronic) and Remi shaking machine for agitating the samples for the required period at a speed of 200 strokes/minute were used. The surface area of the adsorbent particle, porosity and density were measured by using surface area analyzer, mercury porosimetry and specific gravity bottles, respectively.

Material development

Fresh leaves chosen based on their crude fiber content and were obtained from neem (*Azadirachta indica*) trees. The fresh leaves were sun-dried for 3-4 days and then crushed in mixure. The powder was sieved to get various particle sizes, viz. 600, 710 and 850 μm, 1 mm, and 1.4 mm. Leaf powder biomass was frequently washed with water until washing becomes colourless. Then it was filtered and dried in sunlight. This dried powder was used for the adsorption of fluoride ions without any treatment.

Adsorption studies

Adsorption of fluoride ions onto the produced adsorbentwas studied by batch experiments. A stock solution of NaF (221 mg/l) was used in adsorption experiments. The concentration of F^- was determined by pH/Ion meter 363 (systronics).

pH studies

In order to investigate the effect of pH on fluoride adsorption, the pH of the NaF solutions (100 mg/l) were adjusted to different values between 3 and 10. The initial pH of the solution was adjusted by using 0.1 N HCl or 0.1 N NaOH. Dried adsorbent (0.5 g) was added to 50 ml solution. After adsorption, the pH value providing the maximum fluoride removal was determined (Sujana *et al.,* 2009).

Kinetic studies

The rate of adsorption of fluoride was studied at different time intervals. In kinetic studies, 50 ml NaF solution (100 mg/l) and 0.1 g adsorbent were agitated. The mixture was shaken at140 rpm using a temperature controlled water bath. Batch experiments were repeated for different periods until reaching the adsorption equilibrium.

Equilibrium adsorption studies

The adsorption of fluoride from aqueous solutions by adsorbent was carried out at different temperatures (25, 30, 35, 40 and 45^{0}C). In the experiments, 2.5 g adsorbent samples were mixed with 50 ml solutions of various fluoride concentrations between4 mg/l and 12 mg/l. After adsorption, the concentrations of fluoride remaining unadsorbed were determined.

The amount of fluoride adsorbed per unit adsorbent (mg fluoride/g adsorbent) was calculated according to a mass balance on the fluoride concentration (Y.S. Ho. *Carbon*, 2004), using Equation (1):

$$q_e = \frac{(c_i - c_e) x v}{m} \quad (1)$$

The percent removal (%) of fluoride was calculated using the following equation:

$$q_e = \frac{(c_i - c_e)}{m} x \, 100 \quad (2)$$

Results and discussion

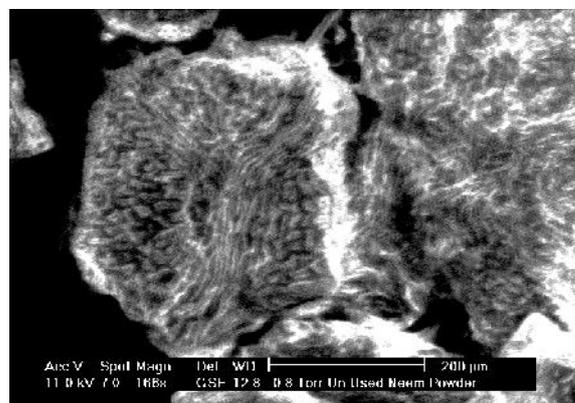### Characterization of the Adsorbents

Physico-chemical characterizations of the adsorbents were shown in Table 1 and these characterizations were done by using standard methods. Table 1 shows that NLP has the higher surface area and total pore volume indicating the roughness of pore walls and increasing of additional active sites. Then more active sites are responsible for adsorption of fluoride ions onto the surface of the NLP. Scanning electron microscopy (SEM) (Figure 1) helps to explain the surface structure of the powder consisting of the fine particles of irregular shape and size on external surface. Figure 1 shows SEM images of NLP having particle size of 200 μm.

Table 1: Physico-chemical Characteristics of NLP.

Physical characteristics	NLP
pH	6.2
EC (mho/cm)	1.5
Bulk density (g/cm^3)	0.86
Solubility in water (%)	0.5
Solubility in acid (%)	0.6
Moisture content (%)	4.2
Ash content	-
BET Surface area	285.6
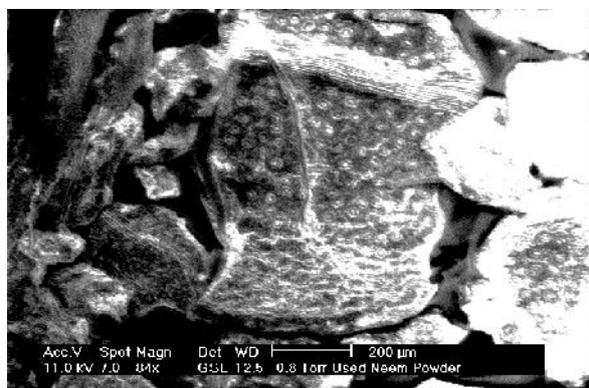
Figure 1. Scanning Electron Microscopy (SEM) images of NLP.

Figure 2. Scanning Electron Microscopy (SEM) images of NLP.

Sorption studies

Successful application of the adsorption technique demands innovation of cheap, nontoxic, easily and locally available material. Bioadsorbents meets these requirements. Knowledge of the optimal conditions would herald a better design and modeling process. Thus, the effect of some major parameters like pH, contact time, amount of adsorbent and concentration of fluoride ions of the uptake on adsorbent materials was investigated from kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the rate and equilibrium data. Experiments were carried out by shaking 0.5 g of adsorbent dose with 50 ml of aqueous solution containing known concentration of fluoride ions and by agitating the samples on Remi shaking machine at a speed of 200 strokes/min. All the experiments were conducted at room temperature ($30 \pm 5°C$).
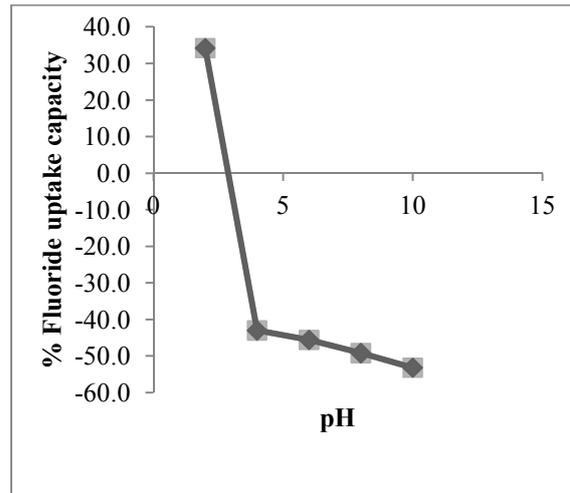
Effect of pH

The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of hydrogen ion concentration was examined at pH values of 2, 4, 6, 8 and 10. This was adjusted by adding 0.5N HNO_3 or 0.1M NaOH with 50 ml of standard solution of fluoride ions for a contact time of 300 min with a dose of 2.5 g bioadsorbent. The influence of pH on the sorption rate is shown in Fig. 3 and effect of pH on adsorption of % Fluoride uptake capacity is graphically represented in Fig. 4. We have observed decrease in the extent of removal of fluoride ions with increase in the pH of the solution.

This was investigated as maximum removal of fluoride 74.25 % at pH 2 and minimum 40% at pH 8.0. Hence further studies were conducted at pH 2.0 values. It is reported that the percentage of adsorption decreased almost linearly between pH values of 2.0 and 8.0 and a maximum removal of fluoride was reported at pH 2.0 in 300 min of contact time. The result may be due to neutralization of the negative charges at the surface of the biosorbents by greater hydrogen ion concentration at lower pH values. This reduces hindrance to diffusion of the negatively charged fluoride ions on to the increased active surface of biosorbents. The similar results have been observed using fish bone charcoal by (Bhargava and Killedar 1991).
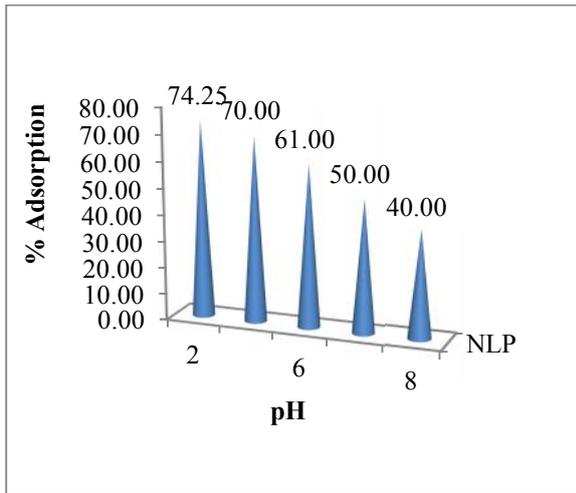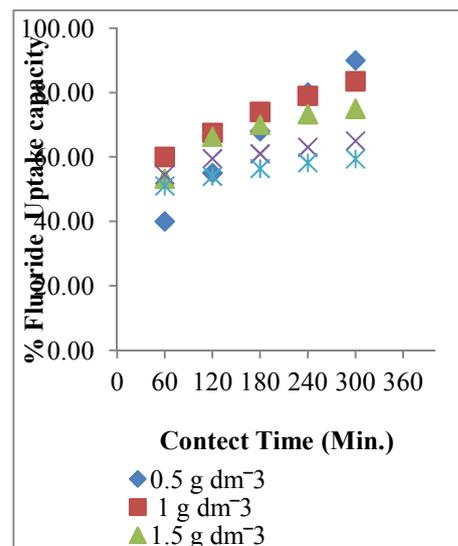
Fig. 3: Effect of pH on adsorption of fluoride on NLP at 300K. Fluoride concentration: 4 mg/L, adsorbent: 2.5 g/L, agitation time: 5 h).

Fig. 4: Effect of pH on adsorption of % Fluoride uptake capacity of NLP at 300K. Fluoride concentration: 4 mg/L, adsorbent: 2.5 g/L, agitation time: 5 h).
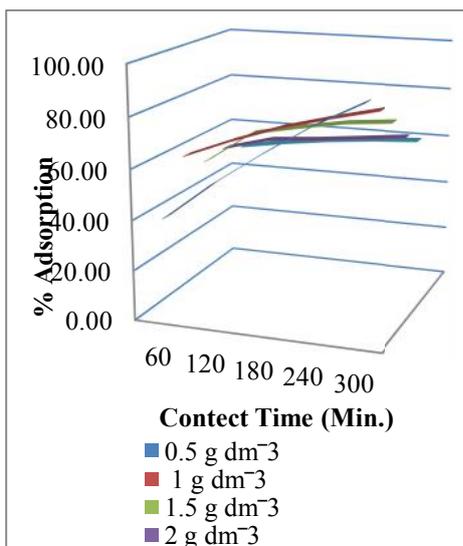
Fig. 5 Effect of agitation time on the adsorption of fluoride on NLP at pH=2, Fluoride concentration: 4 mg/L.

Fig. 6 Effect of agitation time on the % Uptake capacity adsorption of fluoride on NLP at pH=2 Fluoride concentration: 4 mg/L

Effect of contact time

The result shows that the removal of fluoride ions increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material. Preliminary investigations on the uptake of fluoride ions on the adsorbent material at their optimum pH values indicate that the processes are quite rapid. Typically, 74.25 % of the adsorption occurs

within the first five hours of the contact for fluoride ions with an initial concentration 4 mg/l and adsorbent dose of 50 g/l for biosorbents (Fig. 5) and percentage fluoride uptake capacity is graphically represented in Fig. 6. This initial rapid adsorption subsequently gives way to a very slow approach to equilibrium and saturation is reached in 1.5 to 5 h. For further optimization of other parameters, this contact time was considered as the equilibrium time.

Table: 2 Amount of fluoride adsorbed on NLP at 300 K. Fluoride concentration 4.0 mg/L. (Data inside parentheses give percentage adsorbed.)

Contact Time (min.)	Amount adsorbed in mg/L for NLP dose of Adsorbent				
	0.5 g dm$^-$3	1.0 g dm$^-$3	1.5 g dm$^-$3	2.0 g dm$^-$3	2.5 g dm$^-$3
60	3.60(10.00)	2.80(30.00)	2.40(40.00)	1.82(54.50)	1.45 (63.75)
120	3.45(13.75)	2.65(33.75)	2.01(49.75)	1.68(58.00)	1.30 (67.50)
180	3.32(17.00)	2.52(37.00)	1.90(52.50)	1.56(61.00)	1.18 (70.50)
240	3.20(20.00)	2.43(39.25)	1.80(55.00)	1.48(63.00)	1.09 (72.25)
300	3.10(22.50)	2.33(41.75)	1.75(56.25)	1.40(65.00)	1.03 (74.25)

Effect of adsorbent dose

From Fig. 7, it is observed that the removal of fluoride ions increases with an increase in the amount of adsorbent. For all these runs; initial fluoride ion concentration was fixed at 4 mg/l. The amount of adsorbent dose was varied between 10 and 50 g in aqueous solution at their optimal pH values. Results showed that adsorbent was efficient for maximum removal of 74.25% was observed at 50 g, at a room temperature of 29 ^{0}C. Whereas the fluoride ions uptake capacity decreases with an increase in the amount of adsorbent (Fig. 8).
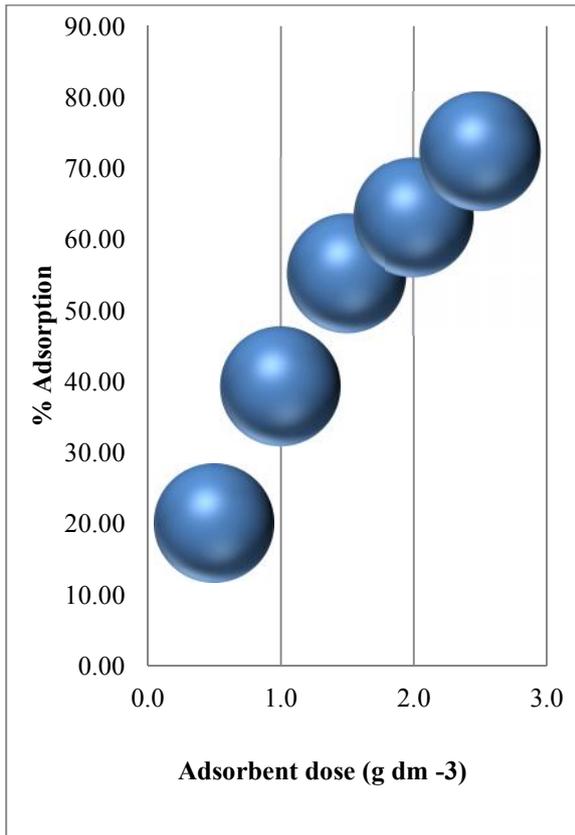
**Fig. 7 Effect of adsorbent dose on the adsorption of fluoride on NLP at pH=2, Fluoride concentration: 4 mg/L.**
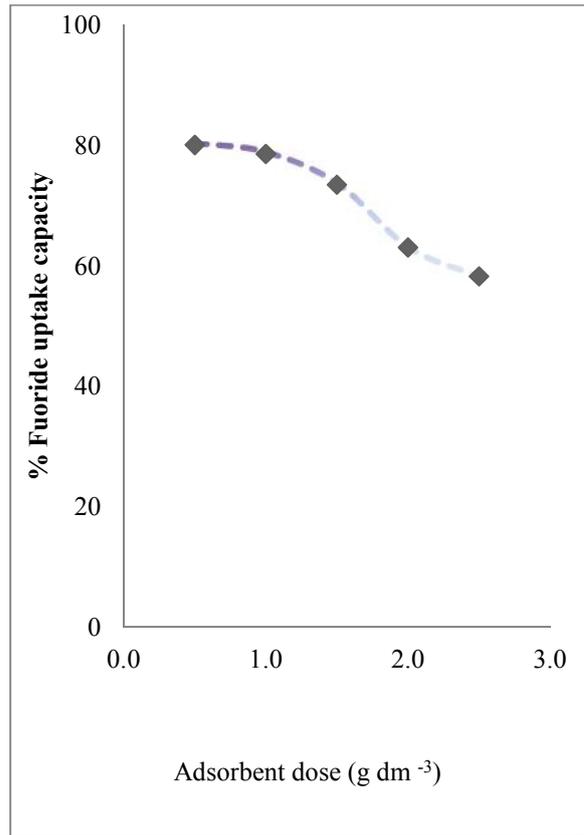
Fig. 8 Effect of adsorbent dose on the % Fluoride uptake capacity of NLP at pH=2, Fluoride concentration: 4 mg/L.

Effect of initial adsorbate concentration

For a strictly adsorptive reaction, in the optimized period of contact, the rate varies directly with the concentration of adsorbate. The capacity of the adsorbent materials gets exhausted sharply with increase in initial fluoride ion concentration (Fig. 9).The adsorption capacity (Fig. 9) of bioadsorbents was systematically studied by varying the initial concentration of fluoride ions between 2 and 15 mg. The percent removal of fluoride ion is a function of initial concentration at different initial pH values. Bio adsorbents may be seen fairly active in reducing fluoride ions from 100% to 40% when the initial concentration of fluoride ion was increased from 2 to 15 mg/l with a constant adsorbent dose of 10 g/l at pH of 2.0.
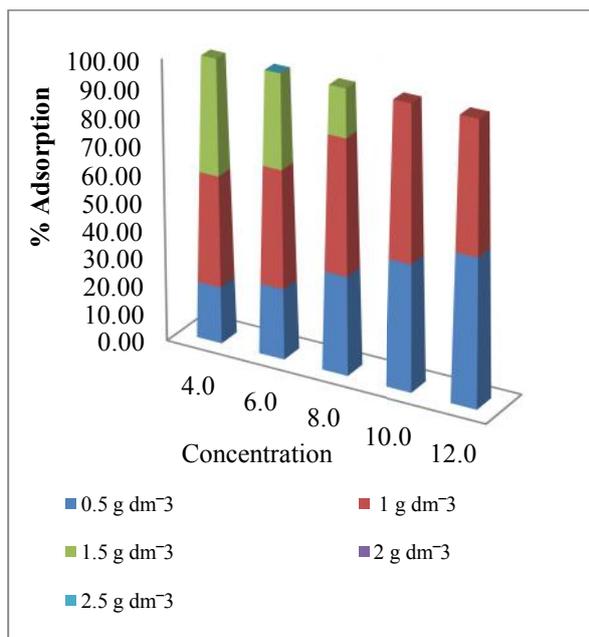
**Fig. 9 Effect of concentration on the adsorption of fluoride on NLP at pH=2.**
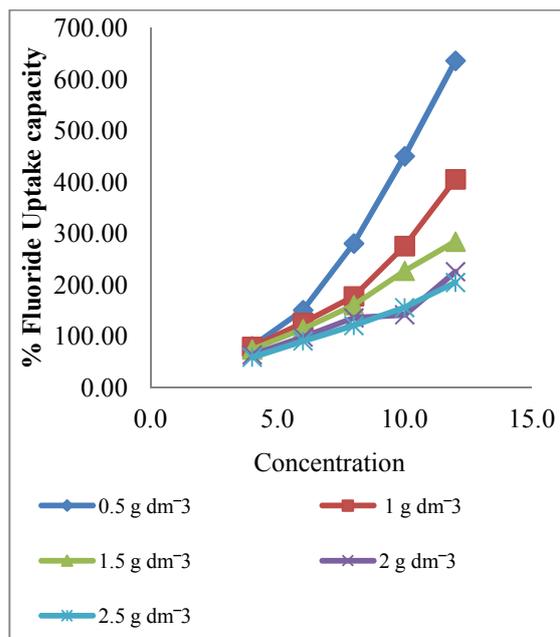
Fig. 10 Effect of concentration on the adsorption of fluoride on NLP at pH=2.

Freundlich equation

Freundlich adsorption isotherm (H.M.F. Freundlich, 1906) based on adsorption on heterogeneous surface is the earliest known relationship describing the adsorption equilibrium and is given by,

$$Q = K_{ef} . C^{\frac{1}{n}} \tag{1}$$

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C \tag{2}$$

$$y = 0.3929x + 0.0691$$
$$R^2 = 0.9825$$
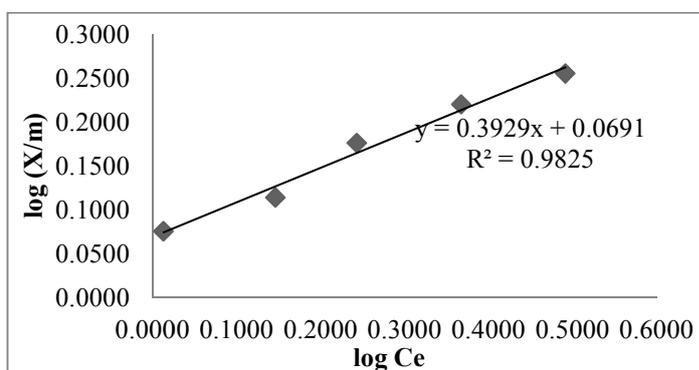
Fig. 11 Freundlich Adsorption isotherm for adsorption of fluoride on Neem Leaf Powder at 300 K and pH 2.0. Contect time 4 hours and fluoride concentration 4 mg/ L.

The linearised Freundlich adsorption isotherm, which is of the form,

$$\log(q) = \log K_f + \frac{1}{n}\log C \qquad (3)$$

Where q is the amount of metal ions adsorbed per unit weight of adsorbents (mg /g), *Kef* and $1/n$ are the Freundlich constants, if $1/n < 1$, bond energyincreases with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$ all surface sites are equivalent. Cis the equilibrium concentration (mg/l). Linear plots of log q vs. log C at different adsorbent doses are applied to confirm the applicability of Freundlich models as shown in Fig. 6. The calculations for Freundlich model for the removal of fluoride ions are shown in Table
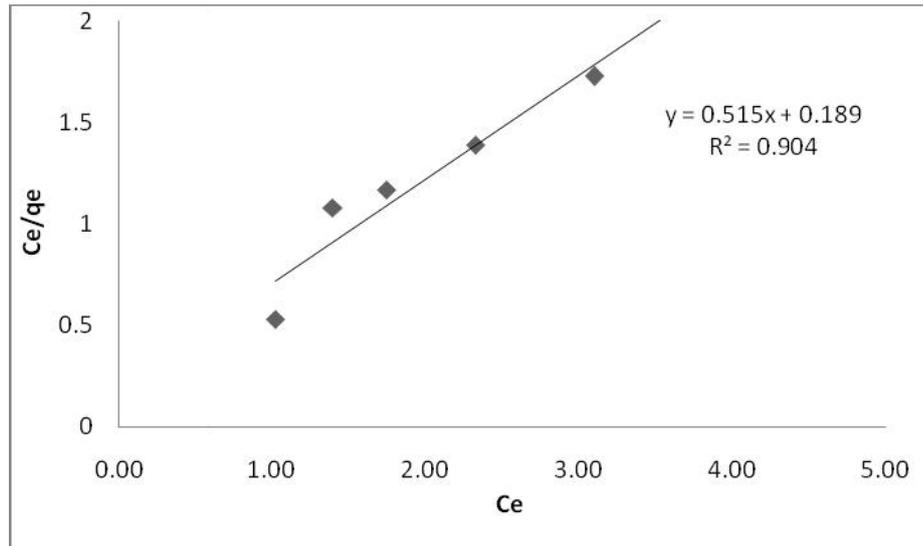
Langmuir isotherm

Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation (I. Langmuir, 1916)is commonly written as,

$$q = Q \, bC \, (1 + bC) \qquad (4)$$

where q is the amount adsorbed (mg/g) and C is the equilibrium concentration of adsorbate (mg/l), Qe and b are the Langmuir constants related to capacity and energy of adsorption, respectively The linear form of the Langmuir isotherm can be expressed as,

$$\frac{1}{q_e} = \left(\frac{1}{Q_e} + \frac{1}{b} Q_0 \; C \right) \qquad (5)$$

$$\frac{C_e}{\left(\frac{x}{m}\right)} = \frac{abC_e}{1 + ab} \qquad (6)$$

Fig. 12 Langmuir Adsorption isotherm for adsorption of fluoride on Neem Leaf Powder at 300 K and pH 2.0. Contact time 4 hours and fluoride concentration 4 mg/L.

Stants band Qo *are* calculated from the slope and intercept with Y-axis. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and describe the type of isotherm defined by,

$$R = 1 + (b\, C_0) \qquad (7)$$

Where *b* and *Co* are terms appearing in Langmuir isotherm. From Figures 6 and 7 it is found that the R^2 value for Langmuir model is near to nity and hence the process of defluoridation using treated biosorbents follows the Langmuir isotherm well. Table gives the calculations of Langmuir model for the removal of fluoride ions and the various constants of this model.

Table 3 : Langmuir and Freundlich Parameters for adsorption of fluoride on NLP.

Freundlich Data		Langmuir Data		Freundlich Constants		Langmuir Constants		Correlation coefficients	
Sample Slope (1/n)	Intercept (log k)	Slope (1/Xm)	.Intercept (1/Xm k)R²	n	k	Xm	k R²	Freundlich	Langmuir
0.480	0.583	0.414	0.601	2.08	3.23	2.41	1.23	0.9820	0.9040

Effect of Temperature and Thermodynamic Study

The influence of temperature in adsorption process is very important because increasing the temperature induces a decrease in the adsorption capacity of fluoride on the adsorbent surface. In the present study the sorption of fluoride was monitored at five different temperatures 298, 303, 308, 313, 318 K underthe optimized condition and thermodynamic parameters viz., standard free energy change (ΔG^{o}),standard enthalpy change (ΔH^{o}) and standard entropy change (ΔS^{o}) were calculated (G. Alagumuthu et al., 2010) andare presented in Table 3 (Fig. 10). The negative values of ΔG^{o} indicated the feasibility of the process and the spontaneous nature of fluoride ions onto adsorbents. Figures 9(a) and (b)shows reducing percentage of both fluoride adsorption and adsorption capacity due to increase of temperature beyond 298 K to 318 K. which indicate fluoride adsorption process onto NLP is explained by the exothermic in nature.The negative values of ΔH^{o} indicated the exothermicnature of the sorptionprocess.The positive value of ΔS^{o} showed the increasing randomness at the solid/liquid interfaceduring sorption of fluoride. The results showed the decrease in adsorption capacity of fluoridewith increasing temperature, which is presumably due to control of the adsorption process bydiffusion phenomenon. Thus, the result indicates the exothermicnature of the diffusioncontrolled adsorption process.
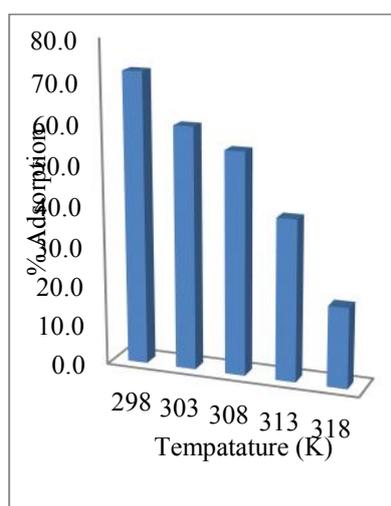
Fig. 13 Effect of temperature on the adsorption of fluoride on NLP at pH=2Fluoride concentration: 4 mg/L, contact time 4 hrs. and adsorbent dose of 2.5 g/l.
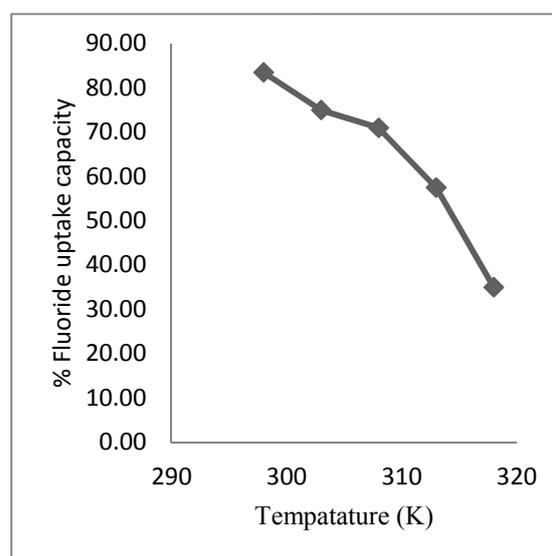
Fig. 14 Effect of temperature on the fluoride uptake capacity of NLP at pH=2, Fluoride concentration: 4 mg/L, contact time 4 hrs. and adsorbent dose of 2.5 g/l.

Table 5. Thermodynamic parameters of fluoride adsorption onto NLP.

Thermodynamic parameters	Temperature (K)	NLP
ΔG^0	303	−7.792
ΔH^0 303	−82.33	
$\Delta S^0$303	−0.246	

Disposal of exhausted adsorbent materials

It is necessary to separate fluoride ion before its disposal. The exhausted adsorbent materials need to be dried and burned. The resultant product can be used in the manufacturing of bricks. Using various chemicals such as H_2SO_4 , HCl, HNO_3 , NaOH, EDTA, etc. desorption is possible.

Advantage of low-cost adsorbents over conventional adsorbents

The efficiencies of removal of fluoride ions of various nonconventional adsorbents vary between 50 and 90% depending upon the characteristics and particle size of adsorbent(s).A combination of adsorbents can also be used effectively in defluoridation treatment. Nonconventional adsorbents are relatively cheaper compared to conventional ones and are easily available resulting in savings in cost.Since the cost of these adsorbents is relatively low, they can be used once and discarded. Nonconventional adsorbents require less maintenance and supervision.Separation is possible to segregate the nonconventional adsorbents from the effluents before their disposal.These nonconventional adsorbents can be disposed off easily and safely.Used adsorbents can be reused as a filler material in low lying areas and hence their disposal does not pose any serious problem.

Conclusion

Results show that these low-cost bioadsorbents could be fruitfully used for the removal of fluoride over a wide range of concentrations. Treated biosorbents were observed to be efficient for the uptake of fluoride ions between 2.0 and 10.0 pH. Fluoride removal for a given bio-adsorbent size increased with time attaining equilibrium within 1.5 h. The percentage of fluoride removal was found to be a function of adsorbent dose and time at a

given initial solute concentration. It increased with time and adsorbent dose, but with higher initial solute concentration decreased with time and adsorbent dose. The process of adsorption by treated biosorbents follows Langmuir isotherm, which comprises statistical and empirical data estimated from Isotherm equation. The adsorption capacity of treated biosorbents was studied by varying the initial concentration of fluoride ions between 2 and 15 mg/l. With the largest particle size of 1.4 mm, the amount of fluoride ions adsorbed was found to be 95. With smallest particle size of 600 for an initial fluoride ion concentration of 10 mg/l, 90% adsorption was observed. Small particle size provides more active surface area and hence such results. Treated biosorbents can be disposed off safely by burning after use. Treated biosorbents are locally available and hence involve no expenditure on transportation and have a very low cost for pretreatment. There is no need to regenerate the exhausted treated biosorbents as they are available abundantly, easily, cheaply and locally. Our future work deals with the evaluation and performance of various biomasses for the removal of fluoride.

Reference

Srimurali M, Pragathi A, Karthikeyan J. "A study on removal of fluorides from drinking waterby adsorption onto low-cost materials". *Environ. Pollut*. 99.2 (1998): 285-9.

Mahvi AH, Zazoli MA, Younecian M, Nicpour B, Babapour A. "Survey of fluorideconcentration in drinking water sources and prevalence of DMFT in the 12 years oldstudents in Behshar City". *J. Med. Sci*. 6 (2006): 658-61.

WHO. Guidelines for drinking-water quality: incorporating first addendum to third edition. Vol 1. Recommendations. Geneva; World Health

Wu X, Zhang Y, Dou X, and Yang M. "Fluoride removal performance of a novel Fe–Al–Cetrimetal oxide adsorbent". *Chemosphere* 69.11 (2007): 1758-64.

Tchomgui-Kamga E, Ngameni E, Darchen A. "Evaluation of removal efficiency of fluoride from aqueous solution using new charcoals that contain calcium compounds". *J. Colloid and Interface Sci*. 346.2 (2010): 494-9.

Dobaradaran S, Mahvi AH, Dehdashti S, Ranjbar Vakil Abadi D. "Drinking water fluoride andchild dental caries in Dashtestan". *Iran. Fluoride*. 41.3 (2008): 220-6.

Dobaradaran S, Mahvi AH, Dehdashti S. "Fluoride content of bottled drinking water availablein Iran". *Fluoride*. 40.1 (2008):16-7.

Veeraputhiran V and Alagumuthu G. "A report on fluoride distribution in drinking water". *Int. J.Envir. Sci.,* 1.4 (2010): 558-566.

Alagumuthu G. and Rajan M. "Monitoring offluoride concentration in ground water of Kadayam block of Tirunelveli district, India". *Rasayan J. Chem*., 4 (2008): 757-765.

Jamode A, Sapkal V, Jamode V. "Defluoridation of water using inexpensive adsorbents". *J Indian Inst Sci*. 84.3 (2004):163-71.

Miramontes MP, Bautista-Margulis RG, Pérez-Hernández A. "Removal of arsenic and fluoride from drinking water with cake alum and a polymetric anionic flocculent". *Fluoride*. 36.2 (2003):122-8.

Mondal NK, Kundu M, Das K, Bhaumik R, Datta JK. "Biosorption of fluoride from aqueousphase onto *Aspergillus* and its calcium-impregnated biomass and evaluation of adsorptionkinetics". *Fluoride*. 46.4 (2013):239-45.

Shams M, Nodehi RN, Dehghani MH, Younesian M, Mahvi AH. "Efficiency of granular ferrichydroxide for removal of fluoride from water". *Fluoride* 2010;43(1):61-6.

Telesiński A, Śnioszek M, Smolik B, Malinowska K, Mikiciuk M, Cichocka J, Zakrzewska H. "Fluoride uptake in hydroponic culture by different clones of basket willow, *Salix viminalis* L". *Fluoride* 44.4 (2011):255-9.

Alagumuthu G., Veeraputhiran V. and Venkataraman R. "Fluoride sorption using*Cynodon dactylon* based activated carbon". *Hem. Ind.* 65.1 (2011): 23-35.

A. J. Arulanantham, T. V. Ramakrishna and N. Balasubramanium, "Studies on Fluoride Removal by Coconut Shell Carbon," *Indian J. Environmental Health*. 13. 5 (1992): 531-536.

S. Kumar, A. Gupta and J. P. Yadav, "Fluoride Removal by Mixtures of Activated Carbon from Neem (Azadirachta) and Kikar (Acacia Arabica) Leaves," *Indian J. Chemical Technology* 14.4 (2007): 355-361.

G. Alagumuthu, V. Veeraputhiran and R. Venkataraman, "Adsorption Isotherms on Fluoride Removal Batch Techniques," *Archives of Applied Science Research* 2.4 (2010): 170-185.

S. Chakrabarty and H. P. Sarma, "Defluoridation of Contaminated Drinking Water Using Neem Charcoal Adsorbent: Kinetics and Equilibrium Studies". *International J. ChemTech Research*. 4 (2012): 511-516.

C. Gisele, S. Bazanella, G. F. Silva, A. M. Vieira and R. Bergamasco, "Fluoride Removal from Water Using Combined *Moringa oleifera*/Ultrafiltration Process." *Water*, *Air*, *and Soil Pollution*. 223.9: (2012): 6083- 6093.

American Public Health Association, Standard methods for the examination of water and Waste water, Washington, 14th Edition, 2007.

M. G. Sujana; H.K. Pradhan; S. Anand. *J. Hazard. Mater.* 161 (2009): 120-125.

Y. S. Ho. *Carbon*. 42 (2004): 2113-2130.

D. S. Bhargava and D. J. Killedar, Batch studies of water defluoridation using fish bone charcoal, *Res. J. Waste Process. Chem. Engrs.*63 (1991): 848-858.

H.M.F. Freundlich. *Z. Phys. Chem.* 57A (1906): 385-470.

I. Langmuir. *J. Am. Chem. Soc.* 38 (1916): 2221-2295.

Venkata Naga Baji Tokala, Pankaj Guptha., "Asroption using neem leaves" *Cosmos J. Engineering and Technology. 4.2 (2014): Am. Chem. Soc.* 38 (1916): 2221-2295.