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Research Article

ENHANCED BIOSORPTION OF FLUORIDE FROM DRINKING WATER USING *BRACHIARIADISTACHYA* LEAVES

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ABSTRACT

Fluoride is the major worldwide problem now facing mainly through drinking water.Several defluoridation methods have been adopted but adsorption processes have been found to be most satisfactory. Adsorption process using plant species are advantageous and eco-friendly. So, biosorption processes have been investigated using the plant species Brachiaria distachya.

Brachiaria distachya is an annual grass having a large volume of biomass which grows in tropical regions. Brachiaria distachya leaves (BDL) were used as biosorbent in powdered form for defluoridation. The efficiency of the leaves to remove fluoride from water has been investigated by varying parameters such as contact time, pH, adsorbent dosage, temperature and initial fluoride concentration. The maximum fluoride removal was observed at pH - 6.0 with adsorbent dosage of 8.5 g using 100 mL of water containing 40 ppm of fluoride in 120 minutes. Under these conditions, temperature variation studies were also carried out from 30-60^0 C and the removal efficiency of fluoride was found to be 92.5 % at pH - 6.0 and temperature 60^0 C. The biosorption process is endothermic following both Langmuir and Freundlich isotherms. The fluoride biosorption process follows pseudo first order kinetics. The results showed that the biosorbent used is cost-effective for treating fluoride containing water.

INTRODUCTION

Fluoride has become a major challenge to treat contaminated water to reduce the risk of fluorosis and dental caries[1]. Fluoride is described as double-edged sword because both high and low concentrations affect health [2]. Fluoride contamination of water cannot be prevented; so defluoridation methods have to be employed to supply the safe drinking water. The permissible limit of fluoride recommended by WHO is 0.5-1.5 mg/L[3]. But increasing fluoride containing is mainly due to emissions from industries like phosphate fertilizers, aluminium smelters, brick, cement industries etc., [5]. The only way to overcome fluorosisis treatment of water (defluoridation) which reduces or removes the fluoride in water.

Several methods [6] have been employed fordefluoridation with different principles like adsorption, use of membranes; precipitation followed by filtration etc., each method has its own limitations and advantages. Most defluoridation processes are of high cost and chemicalsused cause adverse effects on health.

Among the defluoridation methods, adsorption with plant species had been used widely because of its high efficiency, low cost, easy handling and ecofriendly nature. So, an attempt has been made for the removal of fluoride in water using the plant species *Brachiaria distachya* which is a grass easily available in all areas.

Brachiaria distachya is a perennial annual grass belonging to poaceae family commonly known as Armgrass millet[7]. It is wide-spread in tropical regions under humid conditions. It is primarily used as forage which acts as a soil binder in soil erosion control and can be used as trap crop to diversify the sorghum ecosystems which results in reduced shoot fly. So far, there are no reports available on this plant species regarding defluoridation. Hence, for the effective removal of fluoride in water, studies have been undertaken using this species.

Experimental

MATERIALS AND METHODOLOGY

Fluoride solution

All the reagents used were of analytical grade. In all the experiments, double-distilled water was used. A stock solution of 1000 mg/L fluoride was prepared by dissolving appropriate amount of sodium fluoride (Merck) in water and all the solutions for removal experiment and analysis were prepared

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by appropriate dilution from the freshly prepared stock solution. The fluoride concentration was measured with a specific ion electrode (ORION4 STAR) using total ionic strength adjustment buffer (TISAB) solutionto maintain pH 5.3 which eliminate the interference of complexing ions. The fluoride samples and the fluoride standard solutions were diluted to 10:1 with a TISAB solution for fluoride measurement [8].

Preparation of biosorbent

The *Brachiaria distachya* leaves (BDL) were collected from low fluoride areasand washed thoroughly with tap water to remove dust particles. Then again washed with double-distilled water and shade dried for 10 days and powdered. The powder was sieved using 4 mm mesh. The powdered material was treated with chloroform to remove the colour of the plant species and later keptin a hot air oven at 100 ^{0}C for 12 hours in muffle furnace. The material was stored in a plastic bottle. This material was referred as biosorbent used in batch studies of fluoride removal.

Characterisationof thebiosorbent

Surface morphology of adsorbent was investigated using Field emission scanning electron microscope (FESEM) to know the sorption sites of fluoride on biosorbent.EDX (Energy dispersive X-ray) analysis was done to know the elemental composition in the adsorbent.

Method of studying fluoride adsorption

The removal studies were carried out by batch method. A known amount of biosorbent and fluoride solution were taken in a 250 mLplastic beaker. The pH was adjusted to the desired value with different pH buffers. The final volume was made upto 100 ml with distilled water. The solution was agitated at constant speed (400 rpm) using a magnetic stirrer at room temperature over a period of time and then filtered. The concentration of fluoride in the filtrate was determined by fluoride ion selective electrode. Several parameters like adsorbent dosage (1.0-12.0 g), contact time (10-180 min), initial fluoride concentration (10-40 mg/L) and temperature (30-60 ^{0}C) were studied using this procedure and the results presented in the Fig.2 to Fig.6.

RESULTS AND DISCUSSION

Characterization of sorbent

Fig.1(a-d) shows the FESEM and EDX of adsorbents before and after fluoride adsorption. The FESEM images before adsorption show that the BDL consists of different sized particles and their surfaces are irregular. After fluoride adsorption, it appears clearly that the fluoride binding sites are converted into large size and rough surfaces. From the EDX data, weight % of fluoride on the biosorbent was found to be 0.70. This indicates that BDL has the capacity to adsorb fluoride.

The pH point of zero charge was determined as per the method described by Mullet *et al.*, [9] and denoted as pH_{ZPC}. The pH_{ZPC} of BDL was found to be 6.8.

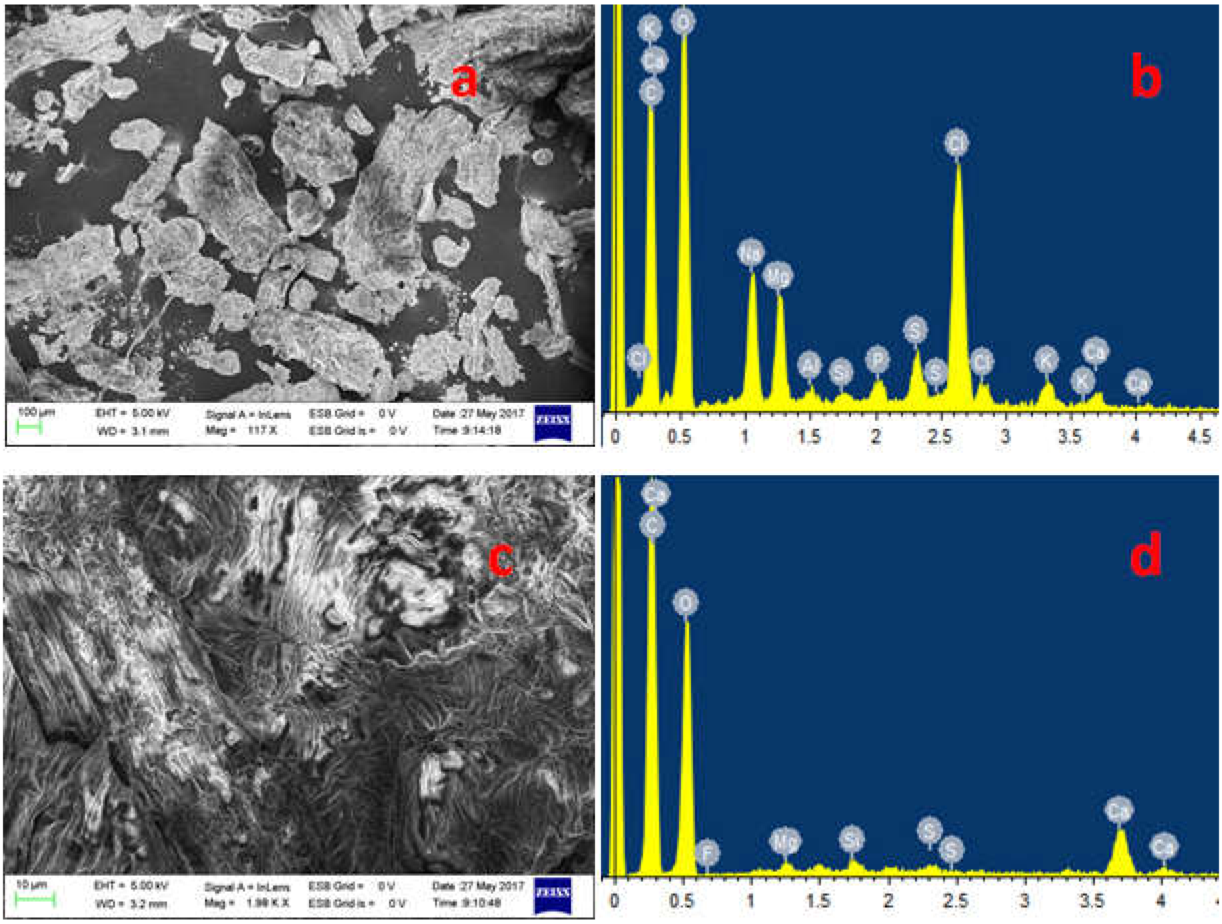

Fig 1 SEM and EDX images of BDL(a, b) before and (c, d) after fluoride treatment $pH_{ZPC}$of an adsorbent

Effect of various parameters on the adsorption of fluoride

Effect of contact time

Batch adsorption studies were carried out using the concentration of 10 ppm of fluoride solution with 0.5 g of adsorbent dosage at 30^0C and at pH-7 as a function of time to evaluate the extent of fluoride removal. The adsorption process was found to attain equilibrium in 120 minutes. The percent of fluoride removal for 10, 20, 30 and 40 ppm were found to be 95.5, 93.9, 88.0 and 87.1 %respectively. These results are presented graphically in Fig.2a.

Effect of pH solution on adsorbent

Effect of pH on adsorption was studied using 20 mg/L fluoride and 0.5 g of adsorbent, varying the pH from 2 to12 at 30 ^{0}C and the results are represented graphically in Fig.2b. The adsorption of fluoride was found to increase with increasing pH reaching a maximum of 92.4 % at pH-6.0 and then decrease with further increase in pH. Therefore, all experiments were conducted at pH-6.0.

Effect of temperature on adsorption process

Effect of temperature on fluoride adsorption was studied using 20 mg/L fluoride and 0.5 g of adsorbent at pH 6, varying the temperature from 30 to 60 ^{0}C and the results are represented in Fig.2c. The adsorption was found to increasewith increase in temperature, the highest adsorption being96.6%.

Effect of adsorbent dose on the adsorption process

The effect of adsorbent dosageon fluoride removal was studied at pH 6 at a temperature of 60^0C and a fluoride concentration of 20 ppm using100 mL of solution. The removal efficiency was found to increase from 68% to 94.95% with increase in adsorbent dosage from 1.0 to 10.0 g/L. This increase is due to availability of more active sites and larger surface area at higher dosages. It was found that further increase in dosage of the adsorbent beyond 10.0 ghas no effect on the adsorption capacity probably because all the fluoride was adsorbed.

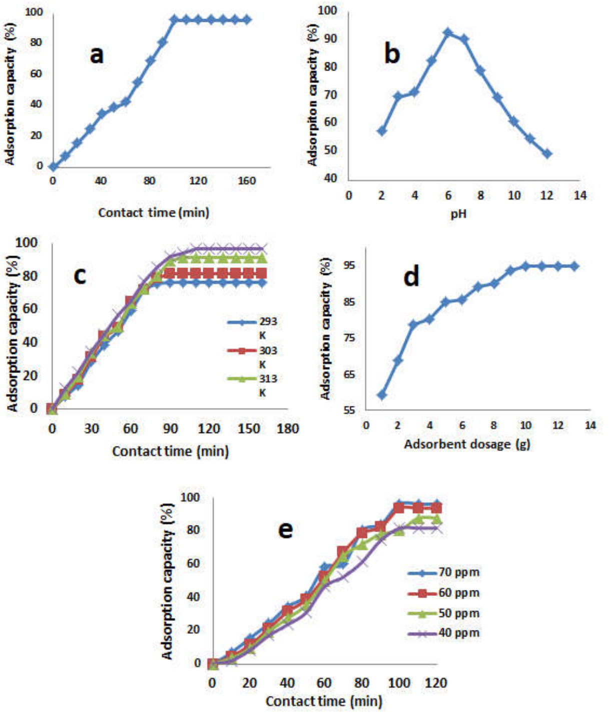

Fig 2 Effect of (a) Contact time, (b) pH, (c) Temperature, (d) Adsorbent dosage and (f) F^- concentration

The effect of adsorbent dosage on fluoride adsorption is depicted graphically in Fig.2d.

Effect of initial fluoride on the adsorption process

The effect of initial fluoride concentration on adsorption capacity of the biosorbent was being studied keeping pH, contact time and adsorbent dosage at their optimum values of 8, 60 min, 3.0g/L respectively varying the initial fluoride concentration from 40 mg/L to 70 mg/L.The results indicated that the percentage removal of fluoride decreases as the concentration of fluoride in solution increases. This may be due to the fact that for a fixed adsorbent dosage, the total available adsorption sites are limited, thereby causing lesser adsorption at higher fluoride concentrations. These results are represented graphically in Fig.2e.

Adsorption isotherms

Batch study results were applied to the linear form of Langmuir isotherm (Eq.1) which indicates the monolayer adsorption process.

$$Ce/q_e = (1/q_m)Ce + 1/K_Lq_m \qquad \text{(Eq.1)}$$

Where q_e isthe adsorption capacity at equilibrium, K_L is a Langmuir adsorption constant, q_m is the maximum adsorption capacity and Ce is the equilibrium concentration of solute. Separation factor, R_L value is 0.82 which is between 0 to 1 indicates the fluoride adsorption onto BDL is favourable.

The data were fitted to Freundlich isotherm (Eq.2) which assumes that the adsorbent forms heterogeneous adsorbing surfaces [11].

$$\log q_e = \log k_f + (\log C_e)/n \qquad \text{(Eq.2)}$$

Where, k_f is the sorption capacity and 1/n is adsorption intensity. The 'n' value obtained is positive in the above equation indicating favorable biosorption. Correlation coefficients, r^2, indicate that the data pertaining to biosorbent fitted reasonably well to Langmuir isotherm represented in Fig.3 a indicating a significant role of surface process in fluoride removal by biosorbent.

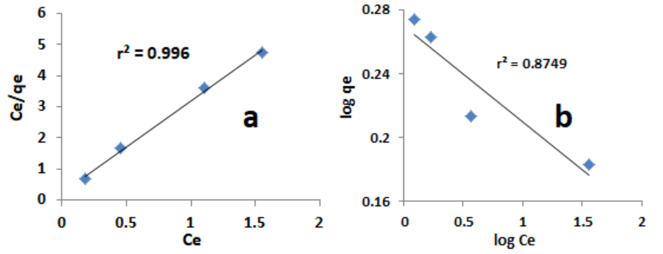

Fig 3 (a) Langmuir and (b)Freundlich isotherm

Table1 Adsorption isotherms

Isotherm	Parameters	Temperature (K)			
		293	303	313	323
Langmuir	q_m(mg/g)	0.26	0.33	0.51	0.65
	K_L (L/mg)	3.86	2.66	1.42	1.07
	R_L	0.49	0.53	0.57	0.58
	r^2	0.940	0.938	0.934	0.926
Freundlich	n	0.92	1.0	1.05	1.19
	k_f	0.43	0.18	0.21	0.27
	r^2	0.929	0.921	0.928	0.888

Thermodynamic studies

Van't Hoff plot is used to estimate the thermodynamic parameters namely changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) in the following Eq.3 [12].

$$\ln (q_e/Ce) = \Delta S^0/R - \Delta H^0/RT \quad \text{(Eq.3)}$$

Where R is the universal gas constant and T is the Kelvin temperature. The change in Gibbs free energy, ΔG^0 was estimated by fitting batch study data to the following Eq.4:

$$\Delta G^0 = -RT \ln K_L \quad \text{(Eq.4)}$$

The estimated ΔG^0 was between -0.05 and -1.42kJ/mol indicating the spontaneous nature of adsorption. The net enthalpy change is positive indicating endothermic process and positive entropy change indicates the increase in randomness of fluoride adsorption onto BDL.

Table 2 Thermodynamic parameters

S.No	Thermodynamic parameters	Temperature (K)	Thermodynamic values
1	ΔG(kJ/mol)	293	-1.42
		303	-0.44
		313	-0.39
		323	-0.05
2	ΔH (kJ/mol)		0.35
3	ΔS (J/mol)		1.56

Adsorption kinetics

Adsorption kinetics studies were carried out in order to understand the mechanism of fluoride adsorptionon adsorbents. For this, pseudo-first order and pseudo-second were used. The rate constant (k) for sorption of fluoride, the considered adsorbent was studied by applying the Lagergren rate equation (Eq.3) [13]. For pseudo-second-order model (Eq.4) was applied [14]:

$$\log (q_e-q) = \log q_e - \frac{k_1 t}{2.303} \quad \text{(Eq.5)}$$

$$t/q_t= 1/q_e\ t + 1/k_{2q}e^2 \quad \text{(Eq.6)}$$

where q_e and q (both in mg g^{-1}) are the amount of fluoride adsorbed at equilibrium and at time t, respectively. k_1 (min^{-1}) and k_2 (g.mg^{-1} min^{-1}) are the kinetic rate constants of pseudo first and second order models respectively and the results are presented in Table-3. The results show that pseudofirst order model fits better than the pseudo second order model. By increasing concentration, rate constant decreases, this may be due to sufficient sites available for adsorption.The results pertaining to pseudo first and second order kinetic models are presented in Fig.4 (a, b). This suggests that the adsorption of fluoride onto the biosorbent was mainly through physisorption.

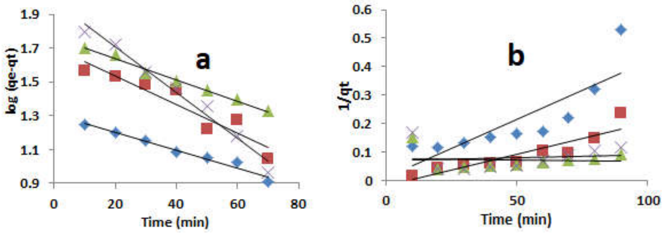

Fig 4 Rate order kinetics (a) Pseudo first order and (b) pseudo second order kinetic models

Table 3 Kinetic models for fluoride adsorption

Kinetic model	Parameter	Kinetic model values
Pseudo first order	q_e	20.2
	$k_1(min^{-1})$	1.1×10^{-2}
	r^2	0.971
Pseudo second order	q_e	454.5
	k_1 (g mg^{-1} min^1)	2.6×10^{-4}
	r^2	0.819

Activation Parameters

The increase in pseudo first order rate constant with increasing temperature may be described by the Arrhenius equation [15].

$$K_1 = A \exp(E_a/RT) \quad \text{(Eq.7)}$$

Where k_1 is the pseudo first order rate constant (min^{-1}), a temperature independent factor (min^{-1}), E_a the activation energy of adsorption (kJ mol^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}) and T absolute temperature (K). Taking the logarithm of (eq.7) gives the following linear relationship:

$$\log k_1 = \log A + (-Ea/R)1/T \quad \text{(Eq.8)}$$

The plot of log k_1 versus 1/T is a straight line showing that the reaction obeys Arrhenius temperature dependence with a correlation coefficient of $r^2 = 0.992$ (Fig. 5). The intercept and slope of the plot give the temperature independent and the energy of activation, E_a is found to be 223.5 kJ mol^{-1}. The increase in activation energy indicates the decrease in rate of the reaction.

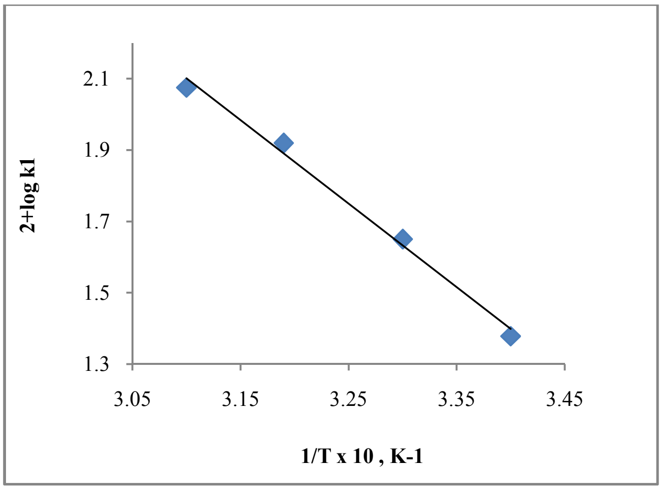

Fig 5 Arrhenius plot of temperature dependence

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