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Defluoridation of contaminated drinking water using neem charcoal adsorbent: Kinetics and equilibrium studies.

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Abstract: Drinking water is often the main source of fluoride intake by humans, especially in areas where their concentrations in groundwater and/or surface water is high. Endemic fluorosis is present in at least 20 states of India, affecting more than 65 million people including 6 million children. Fluoride ion (F) concentrations in India's groundwater vary widely, ranging from 0.01 mg/L to 48 mg/L. Defluoridation of ground water and supply of safe drinking water is the only immediate solution to this problem. The present investigation is an attempt towards a feasible solution.

Batch experimental runs at room temperature were performed to evaluate the adsorption capacity of neem charcoal from aqueous solutions. Adsorption studies for defluoridation on neem charcoal powder showed that the adsorbent were highly influenced by temperature, p^H of the solution, and initial fluoride concentration.

Keywords: Biosorption; Neem Stem Charcoal; pH; Adsorption kinetics; Pseudo-first order; Pseudo-second order;

Introduction:

Management of contaminants such as fluoride is a major public issue. Fluoride enrichment in natural water can occur either by geological processes or from industries[1]. Fluoride of geogenic origin in groundwater used as a source of drinking water is a major concern because fluoride content above permissible levels is responsible for human dental and skeletal fluorosis. Consequently, water sources containing elevated levels of fluoride have to be treated.

Fluorine is in its elementary form a greenish, highly reactive, diatomic gas. It is an electronegative of all known elements and rarely occurs free in nature. It generally combines with other elements to form fluorides and is normally found as the fluoride ion (F^-) in minerals[2]. Fluoride is found in both surface waters and ground water because some fluoride compounds present in the earth's upper crust are readily soluble in water. The average earth's crust abundance is 300 mg kg^{-1} spread in a wide variety of minerals such as fluorspar, rock phosphate, cryolite, apatite, mica, hornblende, and others[3]. The most common fluoride mineral is fluorite (CaF2), a compound with a low solubility that can be present in igneous and sedimentary rocks[4]. The concentration of fluoride in water is normally controlled by the fluorite solubility. In streaming surface freshwater, fluoride concentrations are usually lower than in groundwater because of the shorter contact time between water and rock. The natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature and the action of other chemical elements[5]. The fluoride load in the aquatic environment due to industrial discharge is at least 100-fold higher compared to that which arises due to leaching of fluoride bearing minerals[6]. Fluoride, as a dissolved constituent of drinking water, is perhaps the only substance producing divergent health effects on the consumer depending upon their relative proportions. While a fluoride concentration in the range of 0.8 to 1.20 mg/l is considered to be beneficial, concentration higher than 1.5 mg/l are reported to be harmful to the teeth and bone structure of men and animals. The toxicity of fluoride is influenced by high ambient temperature, alkalinity, calcium and magnesium contents in the drinking water. The drinking water standard for fluoride set by WHO is 1mg/l.

Based on the nature of processes, the defluoridation techniques that have been employed so far are Adsorption and Ion exchange, Precipitation, Electrochemical method and

Membrane technique. However these techniques are not in much use primarily because of their expensiveness, inefficiency or failure in mass scale application. Therefore it is aimed to find a suitable low cost environmentally friendly method for removal of fluoride in the drinking water that could be used by common man. Fluoride removal using synthetic adsorbents are common. Reports on the fluoride removal using algal biomas and tree leaves[7] are available in recent literature. And thus a study on adsorption capacity of untreated Neem stem charcoal (*Azadirachta indica*) has been attempted.

Experimental

Synthesis of adsorbents

In the present study, Neem stem charcoal (*Azadirachta indica)* have been used as adsorbing media. These plants are easily available in this region. Moreover cost of defluoridation is considerably low in the present study and other possible negative impacts i.e. handling of dangerous chemicals, consequences of wrong dosing of chemicals and possible chemical residuals are avoided.

Heat activated Charcoal was prepared from dry stems or timber of neem tree. Charcoal was prepared by charring the dried plant materials at about 100-200°c for about 2h in a muffle furnace, at which all of the material was completely carbonized. The carbonized material was cooled and then grounded in a laboratory blender and made into fine powder. The finely divided powder of neem charcoal is then sorted in dessicator and used for biosorption studies. All chemicals and reagents used for experiments and analyses were of analytical grade. A fluoride stock solution of 100mg/L was prepared by dissolving 0.221g of AR Grade Sodium Flouride (Merck) in 1L of double distilled water at room temperature. The solution was diluted as required to obtain working solution. The initial pH of the working solution was adjusted to 5.0 by addition of 0.1N HNO_3 or 0.1N NaOH solution except experiment examining the effect of pH. Fresh dilutions were used for each study[6-9].

Adsorption Experiments

Batch adsorption experiments were conducted to examine time-dependent sorption behavior and the effects of temperature and solution pH on adsorption performance. Following a systematic process, the adsorption uptake capacity of $F^{/}$ in batch system was studied in the present work.

The data obtained in batch mode studies was used to calculate the equilibrium fluoride adsorptive quantity by using the following expression:

$$q_e = \frac{(C_o - C_e)\,V}{m}$$

where q_e is the amount of adsorbed fluoride onto per unit weight of the biomass in mg/g, V is the volume of solution treated in litre, C_o is the initial concentration of fluoride ion in mg/L, C_e is the residual fluoride ion concentration in mg/L and m is the mass of adsorbent in g/L.[10]

Adsorption studies were carried out at different conditions viz. contact time (30-180 min), pH (2-10), initial fluoride concentration (2-10 mg L^{-1}) and temperature (25, 30, 40 and 55°C). About 0.5 g of the adsorbent was mixed with 100 ml of a desired fluoride solution with known pH and agitated in a mechanical shaker at 100 rpm at a regular interval of time. The solutions were filtered and collected for analysis and fluoride concentration in the solutions was determined. Each determination is repeated three times and the results given were the average values.

Effect of initial ion concentration (for isotherm study) : Equilibrium experiments were carried out by contacting 0.5 g of Neem Charcoal with 100 ml of F^- ion solution of different initial concentrations (2 - 10 mg/L) at pH values of 5.0 at room temperature.

Effect of biosorbent concentration: Batch adsorption tests were done at different concentration of adsorbent from 0.1g to 0.6g at pH 5.0, for a contact time of 20 minutes at room temperature (30°C ± 2°C). The samples were then agitated and filtered and the filtrates were analysed as mentioned before.

Effect of solution pH on biosorption: The effect of pH on the adsorption capacity of Neem stem charcoal was investigated using 100 ml solution of 10mg/L of F ion for a pH range of 2.0 to 10.0 at 30°C. Flasks were agitated on a shaker for 10 minutes to ensure that the equilibrium was reached. Then the mixture was filtered and the concentration of metal in the filtrates was measured.

Results and Discussion

Effect of contact time: The effect of contact time on Fluoride biosorption on NSC was studied and the results were shown in Figure 1.

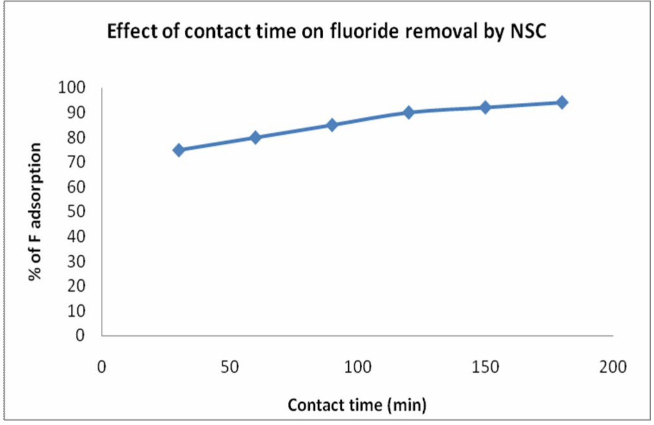

Fig1. Effect of contact time on the percentge removal of fluoride.

From Fig. 1, it was found that the adsorption quantity of Fluoride ion on NSC increases as the contact time increased. The biosorption of fluoride onto NSC was rapid for first 30 minutes (75%) and equilibrium was nearly reached after 180 minutes (94%). Hence, in the present study, 180 minutes was chosen as the equilibrium time. Basically the removal rate of sorbate is rapid, but it gradually decreases with time until it reaches equilibrium. The rate of percent fluoride removal is higher in the beginning due to the larger surface area of the adsorbent being available for the adsorption of the fluoride ion. It is also relevant that, since active sorption sites in a system have a fixed number and each active sites can adsorb only one ion in a monolayer, the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensifies by the fluoride ions remaining in the solution.

Effect of initial metal ion concentration:

Biosorption experiments with NSC were conducted for solutions containing 2mg/L to 10mg/L fluoride ion. As seen in the Figure 2, at lower concentrations of fluoride ion (2mg/L – 6mg/L), biosorption was completed rapidly to about 94-80% success rate, but at higher concentrations biosorption was achieved slowly with a success rate of 75-60%.

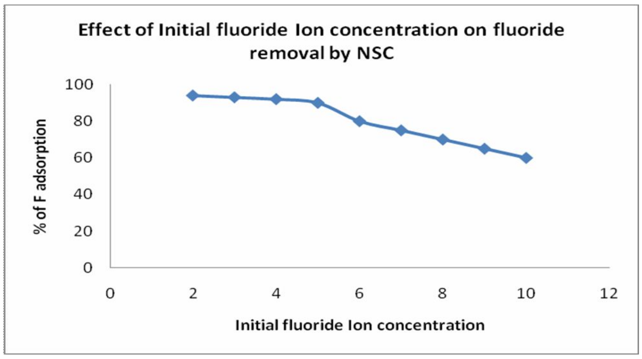

Fig 2 Effect of initial fluoride ion on the percentge removal of fluoride.

At lower concentrations, all fluoride ions present in the solution would interact with binding sites and then facilitated more than 80% adsorption. At higher concentration, more fluoride ions are left unabsorbed in the solution due to the saturation of binding sites. This appears due to the increase in the number of ions competing for available binding sites in the biomass.

Effect of biosorbent concentration:

The percentage removal of fluoride ion increases with increase in NSC doses from 0.1g to 0.5g. There was a non-significant increase in removal of percentages of fluoride when adsorbent dose increases beyond 0.5g. This suggests that after a certain dose of bio adsorbent, the maximum adsorption is attained and hence the amount of ions remain constant even with further addition of dose of adsorbent. The increase in fluoride removal percentage with increase in adsorbent dose is due to the greater availibility of the exchangeable sites or surface area at higher concentration of the adsorbent.

Effect of solution pH:

The pH of the solution is perhaps the most important parameter for adsorption. To understand the adsorption mechanism, the adsorption of fluoride as a function of pH was measured and the result are shown in Figure 3.

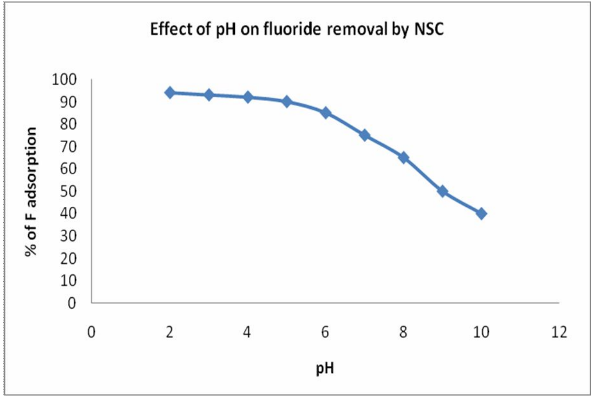

Fig 3 Effect of pH on the percentge removal of fluoride.

Fluoride removal recorded its minimum values at pH 10.0. There was an increase in biosorption capacity of the biomass with decrease in pH from 10.0 to 5.0 and showed marginal increasing trend from pH 4.0. In lower pH values, occupation of the negative sites of the adsorbent by H^+ and H_3O^+ ion leads to reduction of vacancies for fluoride ion and consequently causes decrease in fluoride ion biosorption. As the pH was raised, the ability of the ions for competition with H^+ and H_3O^+ ions was also increased. Although the sorption of fluoride ions raised by growing pH, further increment of pH caused declining in adsorption due to the competition of the hydroxyl ions with the fluoride for adsorption.

Isotherm Study:

Langmuir Isotherm: Defluoridation capacity of NSC was evaluated using the Langmuir and Freundlich adsorption isotherms. Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface is given by the equation:

$$q_e = \frac{q_{\max} bC_{eq}}{1 + bC_{eq}}$$

where qe is the amount of fluoride adsorbed per unit weight of the sorbent (mg g−1), Ce is the equilibrium concentration of fluoride in solution (mg L−1), q_{max} is the amount of adsorbate at complete monolayer coverage (mg g−1) and gives the maximum sorption capacity of sorbent and b (Lmg−1) is Langmuir isotherm constant that relates to the energy of adsorption. Langmuir isotherm constants, viz., q_{max} and b were calculated from the slope and intercept of the linear plot of Ce/qe vs Ce.[10,11]

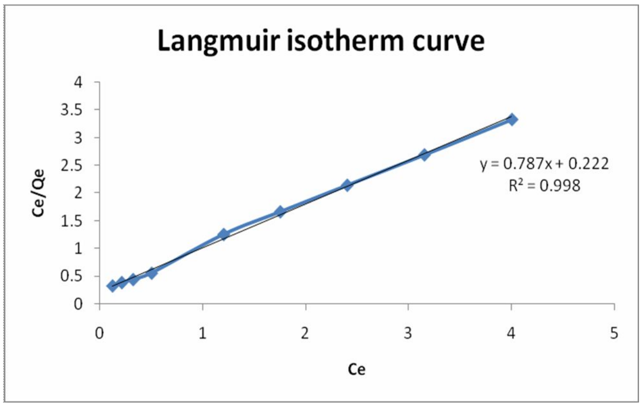

Fig 4 Langmuir Isotherm Curve

The essential characteristics of Langmuir can be explained in terms of dimensionless constant separation factor (R_L), defined by:

$$R_L = \frac{1}{1 + bCo}$$

Where b is the Langmuir constant and C_o is the initial concentration of metal ion. The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L=0), favourable ($0 < R_L < 1$), linear (R_L=1) or unfavourable (R_L>1). The R_L were found to be 0.086 to 0.027 for concentrations of 2 – 10 mg/L $F^/$.

Freundlich isotherm: The Freundlich isotherm in its linear form is represented by:

$\log qe = \log K_f + 1/n \log Ce$,

where qe is the amount of fluoride adsorbed per unit weight of the sorbent (mg g^{-1}), Ce is the equilibrium concentration of fluoride in solution (mg L^{-1}), K_f is a measure of adsorption capacity and $1/n$ is the adsorption intensity. Freundlich isotherm constants of the sorbent were calculated from the slope and intercept of the linear plot log Ce/qe vs. log Ce[10,11].

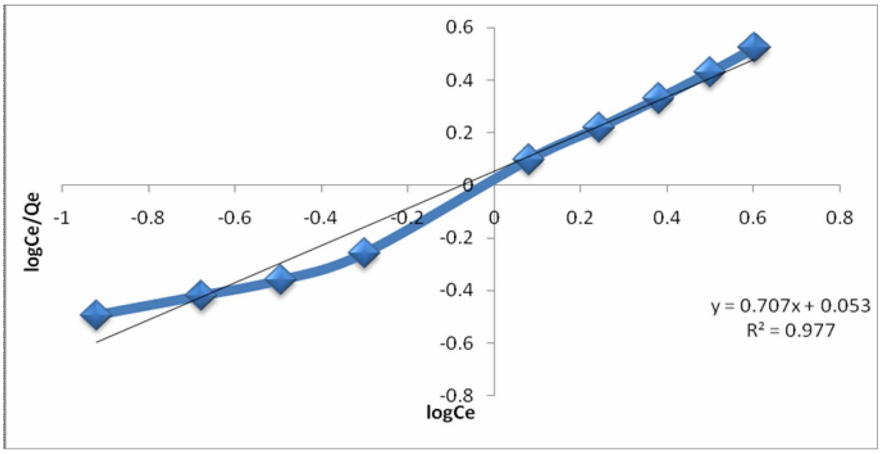

Fig 5 Freundlich Isotherm Curve

Table 1: Isotherm parameters for fluoride adsorption on NSC

Langmuir isotherm			Freundlich isotherm		
b (L/mg)	q_{max}(mg/g)	R^2	K_f	n	R^2
3.55	1.27	0.998	1.13	1.414	0.977

The higher values of R^2 indicate the applicability of both Langmuir and Freundlich isotherm.

Adsorption Kinetics of Fluoride: To understand the kinetics of the process, the data was fitted to different rate equations. A general rate expression takes the form $dq/dt = K_n (q_e - q_t)$ eq(A) with *n* being the rate of the process.

Reaction-based models

A pseudo-first-order rate expression, or the Lagergren rate equation, is expressed as

$\ln (q_e - q_t) = \ln q_e - k_1 t$.

where q_e and q_t are the amount of fluoride on NSC (mg g^{-1}) at equilibrium and at time *t*, respectively, and K_1 (min^{-1}) is the first-order rate constant[6]. A plot of $\ln(q_e - q_t)$ against time (*t*) should yield a straight line (Figure 6), and the rate constant K_1 is evaluated from the slope. In the present investigation ,K_1 = -0.019.

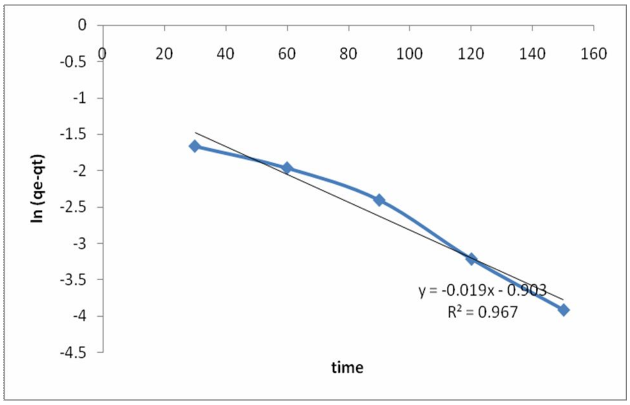

Fig 6 Lagergren equation plot

A pseudo-second-order expression may be derived from eq (A) as

$t/q_t = (1/K_2)(1/q_e^2) + t/q_e$ the boundary conditions of *t* = 0 to *t* = *t* and $q_t = 0$ to $q_t = q_t$ can be applied. A plot of t/q_t against *t* should yield a straight line (Figure 7), with K_2 (g mg^{-1} min^{-1}), the second-order rate constant, obtained from the intercept. Here, K_2= -13.056

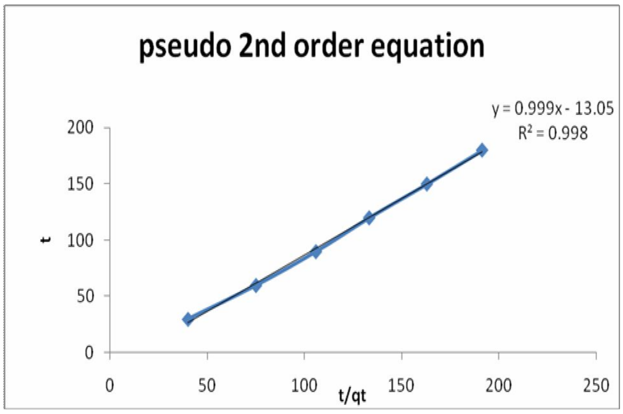

Fig 7 Second-order rate equation plot

Diffusion-based models

In a solid–liquid sorption process the transfer of solute is characterized by pore diffusion or particle diffusion control. The pore diffusion model used here was proposed by Weber and Morris. The linear form of the equation is represented by:

$qt = k_i t^{0.5}$,

where K_i is the intraparticle rate constant (mg g−1 min−0.5). The slope of the plot of *qt* against $t^{0.5}$ will give the value of intra particle rate constant. In the present situation, $K_i = 0.025$.

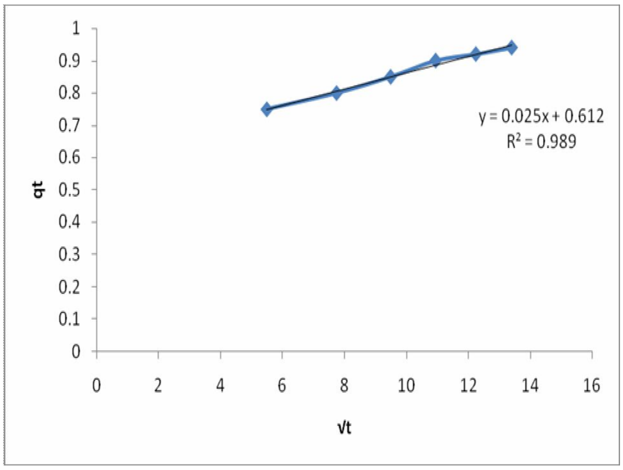

Fig 8 Weber and Morris equation plot

Conclusion :

The neem stem charcoal is found to be an efficient adsorbent for the defluoridation of contaminated drinking water sources. The biosorbent was successful in removal of fluoride ions from aqueous solution of 10mg/l fluoride concentration with about 94% efficiency. Biosorption equilibrium was achieved within 180 minutes. It was observed that the adsorption was pH dependent with maximum adsorption achieved at pH 5.0. Both Langmuir and freundlich isotherm models fits well to the adsorption mechanism. Although regression coefficient of both pseudo first order and pseudo second order plot indicates adherence of both the rate laws but higher regression value of second order plot than the pseudo first order reaction indicates that the adsorption follows the second order rate law. The Webber and Morris plot reveals an initial curved path indicating boundary layer effect followed by a linear path indicating pore diffusion.

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