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Removal of fluoride (F^-) in ground water by living biosorbent

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Fluoride (F^-) contaminated groundwater is elucidated in many parts of the world inclusive India that causing a serious concern on health disorder in human body. Various physico-chemical methods are practiced in the field primarily focusing to remove F^- from water to render fit for human consumption. Sustainable green technology using plant based treatment methods commonly known as phytoremediation to attenuate different metallic contaminants including arsenic has been reported in literatures. However, a limited number of research reports are published so far regarding fluoride attenuation from groundwater by adopting an eco-sustainable rational phytofiltration plant. With this view a laboratory experiment was performed to investigate the uptake and accumulation capacity of F^- by a living aquatic macrophyte. In the present study, living water lettuce (*Pistia stratiotes*) plants were picked up from a nearby shallow pond and grown in Hoagland solution in the laboratory. Batch experiments have been done with different initial F^- concentration and varied amount of biomass doses exposing to fluoride spiked solution. It was observed that, 100 g/L of plant species could effectively remove 44.62% of F^- corresponding to initial concentration of 3 mg/L after 8 days detention time. Different isotherm models were explored to fit with experimental data out of which Freundlich model fitted reasonably well (R^2 = 0.982).

Keywords: Fluoride, phytoremediation, water lettuce, biosorption, isotherm, reaction kinetics.

Introduction

Fluoride level in groundwater worldwide emerges as a challenging threat to mankind affecting serious dental and skeleton disorders. Presence of fluoride in groundwater is geogenic phenomenon due to weathering of fluoride containing rock forming mineral and mixes with sub-surface water by leaching process[1]. In India, fluoride concentration in groundwater has been found exceeding 5 mg/L in many provinces and district levels[2] which is more than permissible level i.e.1.5 mg/L.

Till date, the conventional methods such as Nalgonda technique, using different adsorbents namely activated alumina, bone charcoal, etc. are used for defluridation in water. These methods are pH sensitive and expensive for chemical cost, regeneration and disposal of chemical sludge. Sometimes treated products (sludge) are more toxic than primary pollutant to be disposed. In this context, scientists and researchers put their significant effort to explore an alternative novel removal process which would be economically feasible and technically viable preferably based on sustainable green technology. Phytoremediation is one of the low cost methods, which accomplishes adsorption capacity of aquatic wild plants to remediate polluted water. The concept of plants-based treatment systems to eliminate some contaminants such as, nickel, chromium, cadmium, zinc etc. is elucidated in literature[3]. Toxic metalloid such as arsenic (As) is also reported to be removed from water environment by phytoremediation technique[4]. In the recent time, phytoremediation is proved to be a promising tool to remove F^- from drinking water and this green technology is also helpful for successful achievement towards sustainable development[5]. In view of the above, a laboratory based investigation was carried out primarily aiming to explore the uptake potential and accumulation capacity of F^- by aquatic macrophytes species commonly known as water lettuce (*Pistia stratiotes*). Though these living biomass are competitive with activated alumina that are being used conventionally. However, activated alumina effectively performs well at pH value in the range 5.5–6.5. Hence a subsequent neutralization unit is required for pH correction.

Materials and methods

(B.1) Collection and acclimatization of plants:

Aquatic plants (Pistia sp.) are taken from an adjoining pond of University campus. All plants are washed thoroughly with tap water to clean dirty clay and undesired vertebrates adhered with plants roots. The microphytes are placed in a flat plastic container of 10 L capacity and allowed to grown for necessary acclimatization in laboratory condition in standard hydroponics culture medium (10% Hoagland solution). Once the plants are matured, the adult ones similar in size (60–90 mm long) and 4.0–4.5 g as wet mass were chosen as adsorbent. The back ground water-quality of the pond was checked and no detectable fluoride was evidenced in pond water.

(B.2) Batch study:

Batch experiments were performed in acrylic made troughs of 3 L capacity. The plants were transplanted in separate individual containers with different levels of initial concentration such as 2, 3, 5, 10 mg/L for 10 days of time of exposure. The pH of synthetically prepared water solution was buffered at 6.5±0.2 during the entire study period by the addition of 0.1 (*N*) HCl or 0.1 (*N*) NaOH solutions as necessary. The study was carried out in a temperature controlled room set at 25±2°C for a photoperiod of 10 h per day. Evaporation loss was compensated by adding distilled water. Samples were withdrawn at every 2nd, 4th, 6th, 8th and 10th days of contact period and the measurement of residual fluoride was done by following Standard Methods[6]. Measuring instruments such as expandable ion analyzer (EA 940, Orion Research) and fluoride ion specific electrode (Thermo Scientific, Orion product) are used for this purpose. All this experiments were conducted in triplicate and average was noted.

(B.3) Isotherm study:

Isotherm studies were carried out for different equilibrium data corresponds to initial concentration 2, 3, 5 and 10 mg/L. To find out the most suitable isotherm model that can be used to describe the adsorption process, the analysis of the uptake data have been done by goodness of fitting in following isotherm models:

Freundlich isotherm model:

The relationship between the magnitude of adsorption and concentration can be expressed mathematically according to this model:

$$q = K_F C^{1/n_F}$$

In this relation, q (=X/M) is the amount of adsorbate adsorbed per gram of adsorbent at concentration C mg/L, K_F (mg/g) and n_F are the constant depending upon adsorbate and adsorbent.

Langmuir isotherm model:

From equilibrium approach i.e. rate of adsorption equals to the rate of desorption, Langmuir isotherm model equation is expressed as

$$1/q_e = 1/q_m + 1/(q_m K_L C_e)$$

where, q_e is the monolayer capacity of adsorbent at equilibrium, q_m is the theoretical maximum monolayer capacity and K_L is the Langmuir constant.

(B.4) Kinetic study:

Kinetic experiments are done for an initial concentration of 5.0 mg/L accomplishing varied amount of plant mass in the solution. Samples are tested for residual concentration of F^- in similar way as mentioned above. In order to determine kinetic rate of fluoride removal by water lettuce, experimental results are fitted in four different types of kinetic order model, viz. first, second, pseudo-first and pseudo-second order kinetic models.

The first order equation represented as follows:

$$\ln C_t = \ln C_0 - k_1 t$$

The second order equation represented as follows:

$$1/C_t = 1/C_0 + k_2 t$$

The pseudo-first order equation expressed as follows:

$$\ln (q_e - q_t) = \ln q_e - k'_1 t$$

The pseudo-second order equation[7] represented as follows:

$$t/q_t = (1/k'_2 q_e^2) + t/q_e$$

Optimum kinetic model out of the four models was determined by examining the minimum deviation from best fit lines and maximum correlation coefficient values.

Results and discussion

(C.1) Effect of initial concentration:

The initial concentration of fluoride triggers necessary driving force to overcome all kind of mass transfer resistances between the liquid and solid phases and for this reason a higher initial concentration of fluoride is favorably acted upon increases the overall sorption. A result on time-concentration study for fluoride adsorption by water lettuce is shown in Fig. 1. It is observed that removal shoots up to 44.62% for the initial concentration of fluoride in water was 3 mg/L for 8 days exposure time.

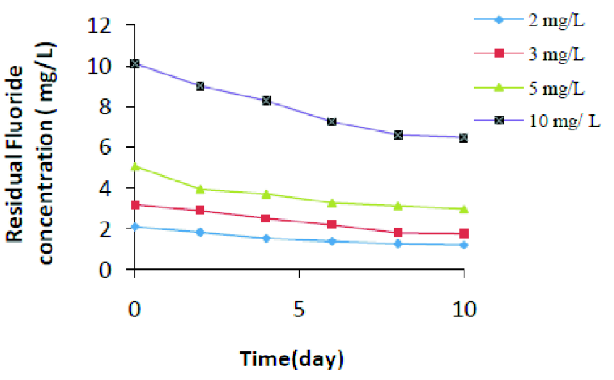

Fig. 1. Fluoride removal by *P. stratiotes* (initial F^- concentration = 2–10 mg/L).

It is observed irrespective of initial concentration, major amount of fluoride removal took place within the first 8 days after which separation was found to be ceased. This indicates that initial concentration level of fluoride imparted a least effect on achieving equilibrium time. From the trend of illustrating curves (Fig. 1), it is also evident that the sorption by water lettuce is a two-step time depended process, i.e. initial fast adsorption during the first 4 days followed by slow rate of sorption until the equilibrium is attained.

(C.2) Isotherm studies:

In this examination phase, equilibrium and isotherm studies are conducted for water lettuce with different initial fluoride concentrations 2, 3, 5 and 10 (mg/L) and adsorbent dosages of 100 g/L. The equilibrium contact time (=8 days) as obtained in the earlier studies[5] is adopted for these experiments. The equilibrium data are used to plot the linear form of following isotherms:

(C.2.1) Freundlich isotherm:

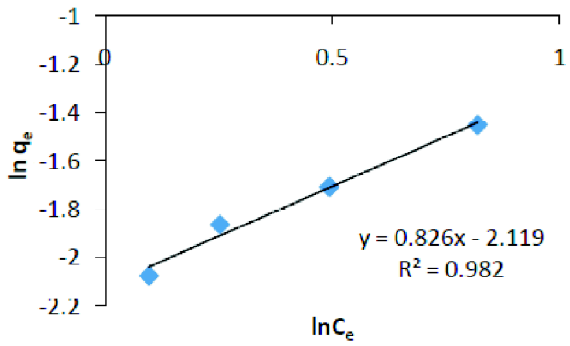

Fig. 2. Freundlich isotherm plot for fluoride uptake by water lettuce.

The linear plots of q_e versus C_e are drawn as shown in Fig. 2. From the above figure, the values of K_f = 0.0076 L/g and $1/n_F$ = 0.827 (n_F = 1.2). The values of K_f and n_F are obtained from intercept and slope of linear plots of Freundlich equation, respectively. The low value of K_f (0.0076 L/g) indicates low adsorption capacity. $1/n_F$ (= 0.827) implies adsorption occurs on heterogeneous surface, but heterogeneity is not too much high as the values are closed to the unity. Further, n_F (= 1.2) lies between one and ten, indicates favorable adsorption[8]. The value of $1/n_F$ below unity implies chemisorption process[9]. As 1< n_F, bond energy decreases with surface density.

(C.2.2) Langmuir Isotherm:

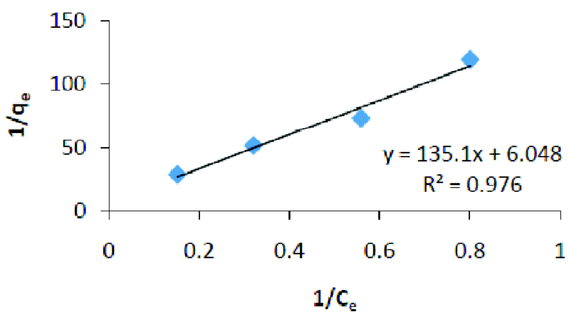

Fig. 3. Langmuir isotherm plot for fluoride uptake by water lettuce.

Langmuir isotherm constants are derived from the plots of $1/q_e$ versus $1/C_e$. q_e = 0.16533 (mg/g) as shown in Fig. 2. The value of K_L is 0.0447 (L/mg) is calculated by plotting equilibrium experimental data (Fig. 3). The value of q_m (mg/g) is theoretical maximum monolayer capacity and K_L (L/

mg) related to the affinity to binding to adsorption sites. The corresponding equation of isotherm models with goodness of fit exhibited in Table 1.

Table 1. Isotherm results

Models	Equation of best fit line	R^2
Freundlich	$\ln q_e = \ln 0.0076 + 0.826 \ln C_e$	0.9824
Langmuir	$1/q_e = 10.16533 + 1/(0.0074\ C_e)$	0.976

(C.3) Biosorption kinetic order study:

The kinetic results are also examined in four kinetic order models. First order model is based on the solution concentration, pseudo-first order equation denotes adsorbent uptake capacity, second order model derived on the basis of solution concentration and pseudo-second order reaction model emerges as solid-phase sorption. Kinetic studies are important because it provides information about the process dynamics and interpret the adsorption rate, detention time and mass transfer parameters such as reaction rate constant. These parameters are useful for the design and operation of any adsorption system in water treatment plants.

(C.3.1) First order kinetic model:

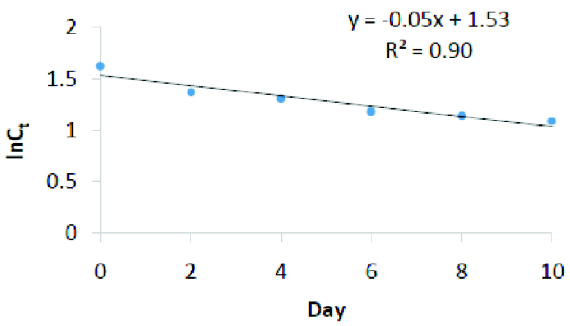

Fig. 4. First order kinetic model for removal of fluoride.

Fig. 4 shows a best fit linear plot between ln C_t with respect to *t* corresponding to first order model. It is revealed that the adsorption kinetics possesses a reasonable trend to follow the first order model.

(C.3.2) Second order kinetic model:

Fig. 5 demonstrates a linear plot between $1/C_t$ against *t* that indicates the reaction rate may be of second order. A best fit line has been drawn which shows that the rate of adsorption follow the second order model reasonably well.

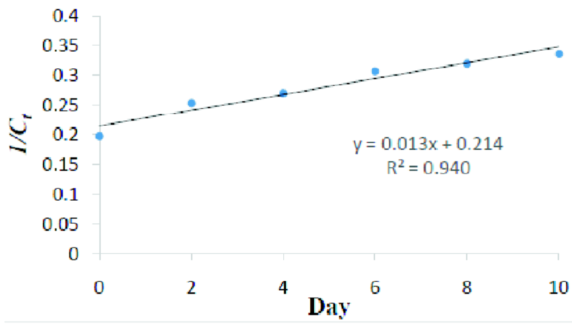

Fig. 5. Second order kinetic model for removal of fluoride.

(C.3.3) Pseudo-first order kinetic model:

The pseudo-first order kinetic equation fitted to a straight line relationship by plotting ln $(q_e - q_t)$ versus *t* as shown in Fig. 6. It is found that the adsorption follow the pseudo-first order model reasonably well.

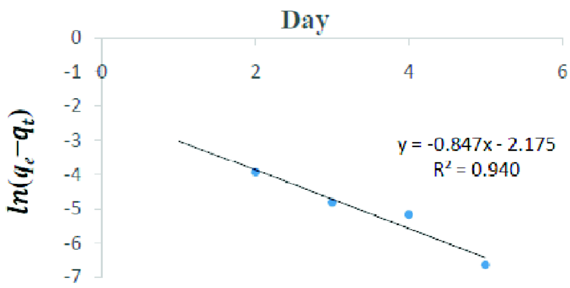

Fig. 6. Pseudo-first order kinetic model for removal of fluoride.

(C.3.4) Pseudo-second order kinetic model:

The equation pertaining to pseudo-second order kinetic is tested as best fit straight line by plotting t/q_t versus *t* as shown in Fig. 7. The R^2 value (0.98) clearly evidenced that the rate of reaction follows pseudo-second order kinetics.

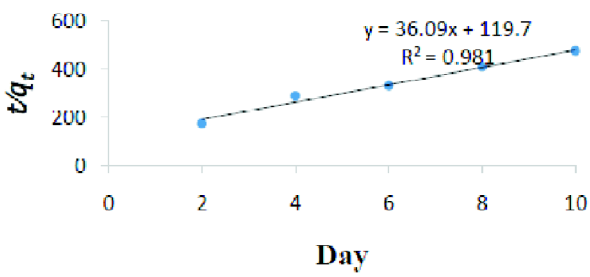

Fig. 7. Pseudo-second order kinetic model for removal of fluoride.

The corresponding equation of kinetic models with goodness of fit is exhibited in Table 2.

Table 2. Results of kinetic order study

Kinetic models	Equation of best fit line	R^2
First order kinetic model	$\ln C_t = 1.53 - 0.05t$	0.900
Second order kinetic model	$1/C_t = 0.214 + 0.013t$	0.940
Pseudo-first order kinetic model	$\ln (q_e - q_t) = -2.175 - 0.8476t$	0.940
Pseudo-second order kinetic model	$t/q_t = 119.7 + 36.09t$	0.981

Conclusion

The batch kinetic study showed water lettuce could fairly remove fluoride from water efficiently. It can remove up to 44.62% fluoride from water when the initial concentration of fluoride in water was 3 mg/L for 8 days exposure time. Isotherm studies depicted that adsorption phenomenon by water lettuce follow Freundlich and Langmuir isotherm models though Freundlich model found to be better suited. Fluoride uptake by water lettuce root also followed pseudo-second kinetic order model. Though the uptake and removal capacity of fluoride is not found very high still the study demonstrated the plant based remediation technology possesses potential future as sustainable method for attenuating toxic pollutant from water environment.

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