Biosorption of fluoride using *Anogeissus dhofarica* – effect of process variables and kinetic studies

Rajamohan Natarajan and Fatma Al Qasmi

ABSTRACT

In this experimental study, a novel biosorbent was synthesized from *Anogeissus dhofarica* and applied for defluoridation under batch-shaking conditions. The influence of process variables, namely initial pH (3.0–11.0), fluoride concentration (50–200 mg/L), biosorbent dosage (0.25–8.0 g/L) and agitation speed (0–600 rpm), on the fluoride uptake was studied. Fluoride uptakes increased with increase in fluoride concentration due to enhanced driving force and decreased with increase in biosorbent dose. An empirical relationship, exponential in nature, was proposed between fluoride uptake and biosorbent dose. The pseudo-second-order rate constant (k_2) was determined as 0.00474 g/ (mg.min) at 303 K with an initial fluoride concentration of 100 mg/L and the rate constant increased with increase in temperature. The activation energy was determined as 6.023 kJ/mol. The chemisorptive nature of fluoride removal was proven through kinetic modeling. The findings of this research proved the feasibility of industrial application of this novel biosorbent for fluoride removal over a wide range of environmental conditions.

Key words | biomass, efficiency, kinetics, sorption

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INTRODUCTION

Pollution of groundwater due to ecological imbalance caused by the release of toxic contaminants is a challenging issue in all the industrialized countries. Fluoride, a dietary requirement for oral hygiene, has become a serious concern due to its excessive release by industries. In addition, fluorine-containing rocks, minerals like fluorite, topaz and their respective host compounds like granite, basalt etc. contribute to the entry of fluoride into the ecosystem (Bhatnagar *et al.* 2011). The World Health Organization has identified fluoride as a priority pollutant along with nitrate and arsenic and reported it to be hazardous above the threshold limit of 1.5 mg/L (WHO 2006). Various industries like glass manufacturing, electrochemical industries, ceramic production units and aluminium smelters are possible industrial sources for fluoride release (Bhatnagar *et al.* 2011; Shen & Schäfer 2014). Excess consumption of fluoride was reported to cause Alzheimer's syndrome, thyroid disorder, bone

disorder, cancer and infertility (TSDR 2003; Dey *et al.* 2004). The mechanism of fluoride influence is through interference with carbohydrate, lipid and protein metabolism (Harrison 2005). Treatment of fluoride-contaminated water has been studied using coagulation with iron(III), alum and activated alumina, reverse osmosis and ion exchange technologies. The applications of these methods are restricted due to disadvantages such as increased operational and running expenses, secondary pollution problems etc. (Bhatnagar *et al.* 2011). A detailed review on defluoridation techniques has discussed all the methods critically and presented that the coagulation method could not reduce fluoride concentrations to less than the permissible levels and that membrane techniques suffer from fouling, scaling and shorter membrane life. High installation cost and expensive maintenance were reported to be associated with electrochemical methods (Ayoob *et al.* 2008). The biological methods

provided an alternative for the removal of fluoride either by active or passive uptake. Biosorption refers to the removal of a contaminant from its source by adsorbing the solute onto an active surface and it differs from conventional adsorption by using an adsorbent generated from living biomass. Biosorption is considered suitable for the removal of ionic contaminants as tailor-made sorbent material can be chosen for the specific removal of pollutants (Park *et al.* 2010; Michalak *et al.* 2013). Moreover, this method involves passive uptake and does not require any special conditions unlike a living biomass application in waste water treatment (Chojnacka 2010; Das 2010). Biosorption of metals using different types of biosorbents has been reported in detail (Wang & Chen 2009). Removal of phosphates from aqueous solution onto *Phoenix dactylifera* L. date palm fibers was studied successfully (Riahi *et al.* 2009). Research on the removal of acid red dye using plant-based biosorbent was reported and the kinetic modeling was completed (Rajamohan *et al.* 2013). With this background, it was understood that the successful application of a biosorbent for defluoridation was determined by the economic feasibility of the process and cheaper availability of the adsorbent. In this research study, a novel biosorbent was synthesized using low-cost locally available plant biomass, *Anogeissus dhofarica*. To date, there is no study available on defluoridation using the above said biosorbent. The effect of environmental parameters, namely initial solution pH, initial fluoride concentration, biosorbent dose and agitation speed on the removal efficiency and uptake was studied. The kinetic mechanism was studied using the pseudo-second-order kinetic model.

MATERIALS AND METHODS

Synthesis and processing of sorbent

Oman is a sub-tropical desert with hot and humid climate and includes more than 1,100 flowering plant species. *Anogeissus dhofarica* is reported as a common tree species found in the Dhofar region (Miller & Morris 1988; Oberprieler *et al.* 2009).The tree leaves were collected, and washed with double distilled water to remove the impurities. The sliced material was sun dried by exposure to sunlight for

3 days and subsequently in a hot air convection oven at 60 °C for 48 h. The dried material was milled into a powder using a blender and sieved to obtain constant-size particles (0.300–0.425 mm).

Chemicals

Stock fluoride solutions were made using sodium fluoride (NaF, Sigma Aldrich). All other chemicals used in this study were AR Grade supplied by Sigma, USA.

Experiments

The influence of operating conditions on defluoridation efficiency was studied by varying the initial pH of the solution, biosorbent dose, initial fluoride concentration and agitation speed. The design of experiments involved varying one parameter a time while the operating parameters were fixed. In the first experimental study, the influence of solution pH was studied in the range of 3.0–11.0 at fixed fluoride concentrations of 100 mg/L, biosorbent dose 4.0 g/L, agitation speed 300 rpm and temperature 303 K. The effect of biosorbent dosage was conducted in the range of 0.25–8.0 g/L at fixed conditions of fluoride concentration, agitation speed and optimal pH. The effect of initial fluoride concentration was studied in the range of 50–200 mg/L and the final set of experiments was performed to study the influence of agitation speed in the range of 0–600 rpm. At fixed intervals of time, samples were collected and the biosorbent particles were removed by filtration. An ion selective electrode was used to analyze the filtered sample for residual fluoride concentrations (Thermo Fisher Scientific 2011). The co-existing ions' interference was nullified using the ionic strength adjustment buffer. All the experiments were conducted in triplicate and their relative standard deviations were in the acceptable range. Fluoride removal efficiency was calculated by Equation (1):

$$\text{Fluoride removal efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

The fluoride uptake was calculated by Equation (2):

$$q_t = (C_o - C_e)V/m \qquad (2)$$

where C_0 and C_e are the initial and equilibrium fluoride concentrations respectively (mg/L); V is the volume of the sample (L) and m is the biosorbent dose (g/L). The pseudo-second-order model (Ho 2006), a popular model, was more convenient to use because of the following advantages: (i) no requirement of assigning an effective adsorption capacity and (ii) no requirement of a prerequisite parameter to estimate the initial adsorption rate. The linearized form of the pseudo-second-order kinetic model is expressed as Equation (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \tag{3}$$

where q_2 (mg/g) is the maximum adsorption capacity, q_t (mg/g) is the amount of fluoride adsorbed at time t, and k_2 (g (mg min)$^{-1}$) is the equilibrium rate constant for pseudo-second order adsorption.

RESULTS AND DISCUSSION

Effect of pH

The variations in the concentrations of the solute pollutants and other co-existing impurities do alter the pH of the waste water. In order to verify the suitability of the biosorbent to function over a wide range of pH, experiments were conducted from pH 3.0 to 11.0. From Figure 1, it was inferred that the fluoride uptake remained approximately closer in the range of 3.0–4.0 and decreased further with increase in
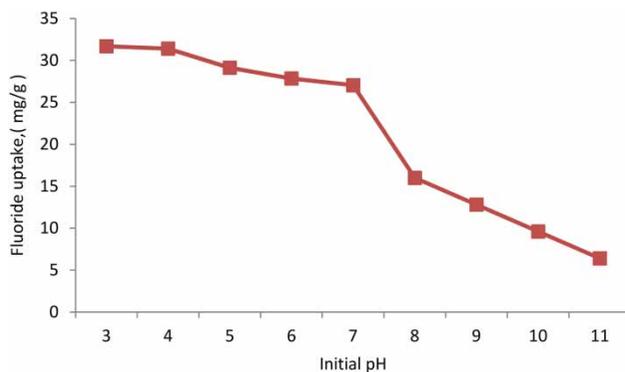

Figure 1 | Effect of initial pH on fluoride removal by *Anogeissus dhofarica* ($t = 90$ min, $C_0 = 100$ mg/L, $m = 4.0$ g/L).

pH. The maximum uptake attained was 31.68 mg/g at pH 3.0 and decreased to 6.4 mg/g at pH 11.0. The better fluoride uptakes obtained in the acidic pH range were related to the estimated zeta potential value of 4.67 using the batch equilibrium method. The surface charges are positive when pH < 4.67 and this factor contributed to the better interaction between positive active sites and negative fluoride ions. Moreover, the presence of excess hydroxide ions under alkaline conditions created competition with fluoride cations for sorption. Fluoride removal using $KMnO_4$-modified activated carbon derived from steam pyrolysis of rice straw reported a similar influence of zeta potential on the uptake (Daifullah et al. 2007). Adsorption of fluoride using carbon derived from sargassum species reported a variation of surface charges at pH values less and greater than zeta potential values (Yu et al. 2015). Studies on removal of acid red dye have reported similar competition between solute ions and ions in solution due to pH changes (Rajamohan et al. 2013). The optimal pH was identified as 4.0, which yielded an uptake of 31.4 mg/g, and all experiments conducted for evaluation of the effects of other parameters were conducted at optimal pH.

EFFECT OF INITIAL METAL CONCENTRATION

Depending on the ecological conditions, the rate of fluoride released by rocks can vary and the fluctuations in fluoride loading into the aquatic system are a variable component. Industrial release too can have variations due to process inefficiencies. The ability of the biosorbent to handle a wide range of fluoride concentrations was studied at four different initial concentrations, namely, 50, 100, 150 and 200 mg/L. The rate of removal always showed a steep increase during the initial contact period which was related to the complete availability of surface active sites for fluoride ions and the number of available sites decreased with time due to progressive occupancy of the sites. From Figure 2, it was observed that the fluoride uptake increased from 18.2 mg/g (at 50 mg/L fluoride concentration) to 50.0 mg/g (at 200 mg/L fluoride concentration). The fluoride uptake values observed at 100 mg/L and 150 mg/L fluoride concentrations were 31.4 and 40.8 mg/g respectively. The uptake values were found to vary in direct proportionality with
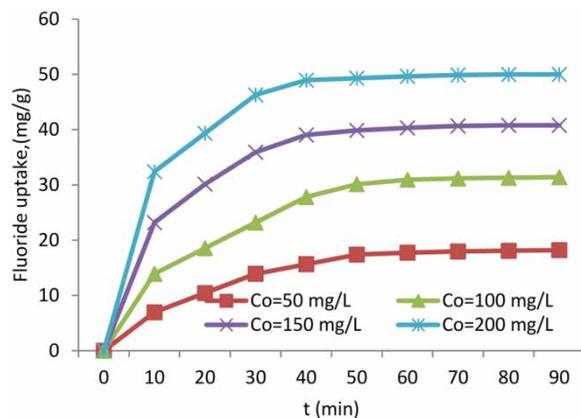
Figure 2 | Effect of initial fluoride concentration on uptake by *Anogeissus dhofarica* ($t = 90$ min, pH $= 4.0$, $m = 4.0$ g/L).

fluoride concentration. This increase in uptake at higher fluoride concentrations was attributed to the availability of an enhanced concentration difference resulting in better interactions of adsorbent surface and adsorbate ions. The driving force for mass transfer is high at higher initial fluoride concentrations and helped in overcoming the resistance. Adsorptive removal of metal ions on barley straw ash reported an increase in metal uptake with increase in metal concentration (Arshadi *et al.* 2014).

EFFECT OF ADSORBENT DOSAGE

The quantity of adsorbent required to achieve a desired removal efficiency is an important design variable. In this set of experiments, the biosorbent dosage was varied in the range of 0.25–8.0 g/L and the corresponding fluoride removal efficiencies and uptakes were recorded. As shown in Figure 3, it was observed that the fluoride removal efficiency increased with increase in biosorbent dosage. The removal efficiency attained was 32% at a dose of 0.25 g/L and increased to 92% at a dose of 8.0 g/L. The increase in efficiency with biosorbent dosage was due to the increase in ratio between the number of free sites and fluoride ions. But, the pattern of increase was observed to be different in the ranges of 0.25–4.0 g/L and 6.0–8.0 g/L, which could be due to a saturation effect. On the contrary, the fluoride uptake values decreased with increase in biosorbent dosage. The reason for this decrease was reported to be the aggregation and agglomeration of sorbent particles at
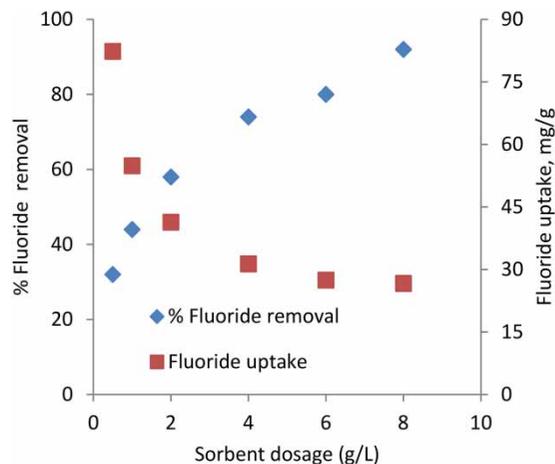
Figure 3 | Effect of *Anogeissus dhofarica* dosage on % fluoride removal and uptake ($t = 90$ min, $C_0 = 100$ mg/L, pH $= 4.0$).

higher doses which led to a decrease in the surface area and an increase in the diffusional path length (Daifullah *et al.* 2007). The best-fit relationship between fluoride uptake and biosorbent dose was proposed ($R^2 = 0.989$) and given by Equation (4):

$$q = 83.77 \, e^{-0.667m} \tag{4}$$

EFFECT OF AGITATION SPEED

Homogeneity of the solution and uniformity in concentration gradient are essential for uniform removal patterns of dissolved solute ions. The effect of agitation speed was conducted from 0 (static conditions) to 600 rpm. The uptake capacity increased in the range of 0–300 rpm and no significant increase was observed in the speed range of 400–600 rpm as is presented in Figure 4. Increase in uptake with speed was related to better mixing and increased contact frequency between sorbent surface and fluoride ions. But at higher speeds of agitation (>300 rpm), the uptakes achieved were less due to shearing of adsorbed ions and vortex formation.
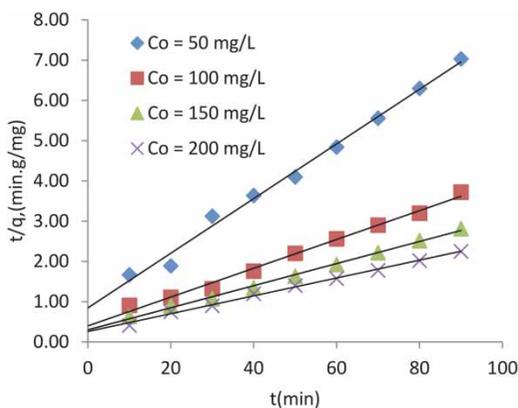
KINETIC STUDIES

The kinetic experiments were conducted over a concentration range of 50–200 mg/L at three different
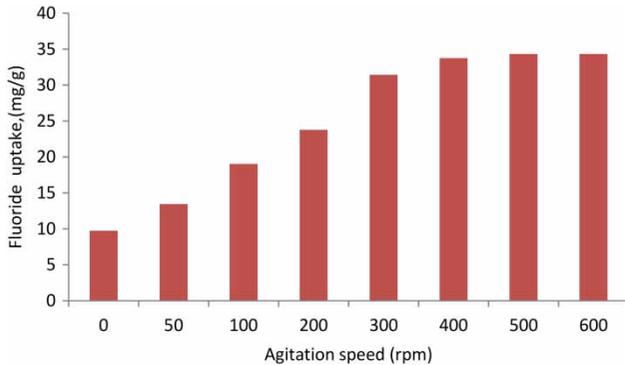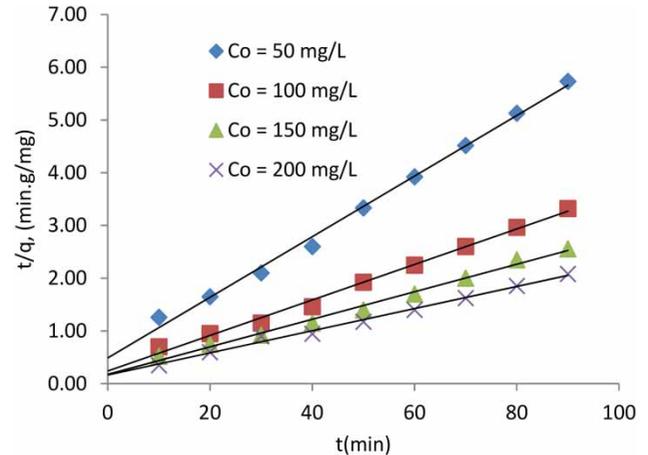
Figure 4 | Effect of agitation speed on fluoride removal by *Anogeissus dhofarica* ($t = 90$ min, $C_0 = 100$ mg/L, $m = 4.0$ g/L, pH = 4.0).

temperatures, namely 298, 303 and 308 K. The linearized form (represented in Equation (3)) was plotted in Figures 5–7, and the model constants, q_2 and k_2, were estimated from the slope and intercept of the lines. The pseudo-second-order model was plotted in its linear form as Figure 5 between t and t/q at 293 K. Similarly, the kinetic data at temperatures 303 K and 308 K were plotted as Figures 6 and 7 respectively. Table 1 presents the kinetic model parameters at different initial fluoride concentrations. Under all the temperature conditions, the values of k_2 decreased with increase in fluoride concentration from 50 to 200 mg/L. The uptake capacities increased with increase in fluoride concentration and the pseudo-second-order model fitted to the entire range of data with comparatively higher values of R^2 (>0.976). At 100 mg/L fluoride concentration, the rate constant (k_2) increased from 3.22×10^{-3} g/(mg.min) to 5.41×10^{-3} g/(mg.min) when the temperature increased from 298 to 308 K. The suitability of the pseudo-second-
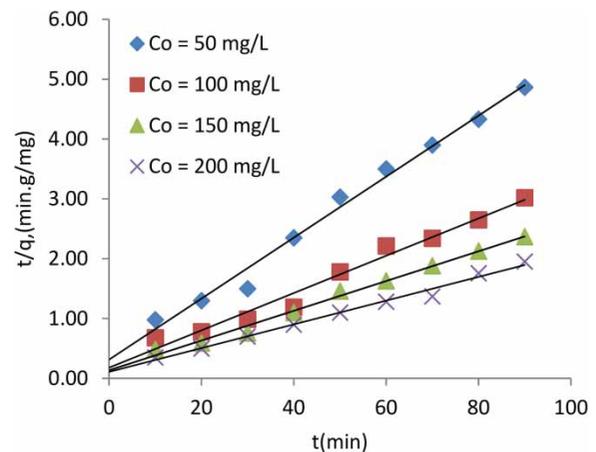

Figure 6 | Pseudo-second-order kinetics plot for the removal of fluoride by *Anogeissus dhofarica* at 303 K.

order model for the experimental data confirmed the validity of the model-based assumption that the rate of occupancy of sorption sites is proportional to the square of the number of unoccupied sites (Yu *et al.* 2015). The mechanism of fluoride removal could be due to chemisorption.

DETERMINATION OF ACTIVATION ENERGY

The activation energy of adsorption was determined using the linearized form of the Arrhenius equation shown in Equation (5):

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{5}$$

Figure 5 | Pseudo-second-order kinetics plot for the removal of fluoride by *Anogeissus dhofarica* at 298 K.

Figure 7 | Pseudo-second-order kinetics plot for the removal of fluoride by *Anogeissus dhofarica* at 308 K.

Table 1 | Kinetic model constants for removal of fluoride

		Fluoride concentration (mg/L)			
Pseudo-second-order model constants		50	100	150	200
$T = 298$ K	q_2 (mg/g)	14.73	27.93	36.49	45.04
	$k_2 \times 10^3$ (g/(mg min))	5.46	3.22	2.50	1.92
	R^2	0.992	0.991	0.997	0.995
$T = 303$ K	q_2 (mg/g)	17.39	29.67	38.31	47.62
	$k_2 \times 10^3$ (g/(mg min))	6.78	4.74	3.82	2.67
	R^2	0.995	0.993	0.992	0.993
$T = 308$ K	q_2 (mg/g)	19.62	32.05	40.32	50.50
	$k_2 \times 10^3$ (g/(mg min))	8.30	5.41	4.49	3.60
	R^2	0.988	0.977	0.990	0.989

where k_2 is the rate constant obtained at different temperatures with the pseudo-second-order kinetic model, E_a (kJ mol^{-1}) is the activation energy, A (g (mg min)$^{-1}$) is the Arrhenius factor, R is the gas constant and T (K) is the solution temperature. The activation energy, estimated from the slope of the best fit line in Figure 8 was found to be 6.023 kJ/mol.

COMPARISON WITH OTHER STUDIES

The modified limestone product has a fluoride adsorption capacity of 6.45 mg/g and the mechanism of removal was physical sorption (Gogoi & Dutta 2016). Removal of fluoride from drinking water by natural stilbite zeolite modified with Fe(III) was reported and the maximum fluoride adsorption capacity was 2.31 mg/g (Sun *et al.* 2011). The maximum
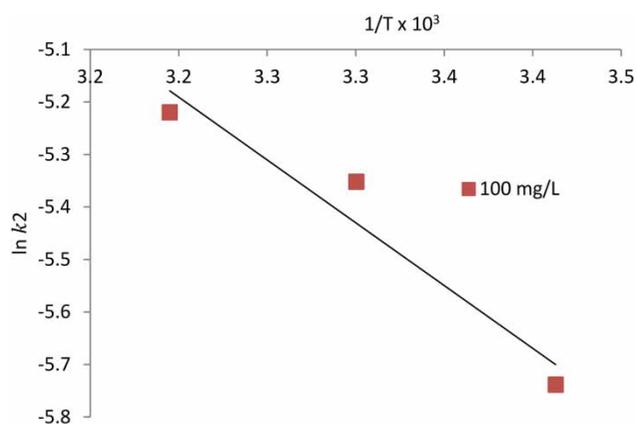
Figure 8 | Arrhenius plot for activation energy.

fluoride uptake by lanthanum-impregnated bauxite was reported to be 18.18 mg/g (Vivek Vardhan & Srimurali 2016). The fluoride uptake achieved in this study was 31.4 mg/g with 100 mg/L initial fluoride concentration at optimal pH 4.0 and biosorbent dosage of 4.0 g/L.

CONCLUSION

This research paper has addressed the application of biosorptive removal for fluoride from aqueous solution. The parametric studies proved that better uptakes of fluoride occurred under acidic pH conditions as the presence of competing hydroxide ions was negligible. The optimal biosorbent dose was found to be 4 g/L and the relationship between uptake and dose was derived. The maximum uptake of fluoride achieved was 31.4 mg/g at an initial fluoride concentration of 100 mg/L. Due to limitations in the availability of active sites, the fluoride uptake decreased with increase in fluoride concentrations. The pseudo-second-order model was fitted to the experimental data and the model parameters were evaluated. Chemisorption was identified as the mechanism of fluoride removal by selected biosorbent. The activation energy of the process was evaluated.

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