OPTIMIZATION OF ADSORPTION PARAMETERS FOR REMOVAL OF FLUORIDE BY ACTIVATED CARBON PREPARED FROM *PROSOPIS CINERARIA* LEAVES

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ABSTRACT

A large population around the world is facing the problem of groundwater toxicants associated with the fluoride and its adverse effects, therefore, number of attempts have been made for the removal of fluoride by some low-cost and environment friendly processes. Bio-adsorbents are one of the promising precursors for the adsorption process which can remove or minimize the various types of toxic organic and inorganic pollutants present in industrial effluents and groundwater. The present study deals with an effective method for fluoride removal by activated carbon prepared by two different processes from *Prosopis cineraria* Leaves through the adsorption methods. A Batch method was conducted for optimizing the adsorption conditions like adsorbent doses, initial fluoride concentration, pH and time etc. Maximum removal efficiency was found to be 85 to 88 percent for equilibrium time of 80 ± 5 min at optimizing pH of 7 ± 0.4 with optimum doses of adsorbent 6.5 ± 0.5 g/l. It was observed that the adsorption obeys more closely to Freundlich isotherm rather than Langmuir isotherm.

KEY WORDS : Ground water, Fluoride, Adsorption efficiency.

INTRODUCTION

Groundwater is the only source for drinking and irrigation purposes in remote areas of the Thar Desert of India. In recent years contamination of ground water has enormously been increased in arid and semi-arid regions of the world (Adimalla, 2019).

The most common problem associated with potable water is identified with the presence of some toxic ions such as Fluoride, Nitrate and Arsenic and is considered as major troublesome pollutants affecting millions of people around the world. Among the above, fluoride was found notorious for its double- edges sword as inadequate consumption associated with dental caries whereas excessive intake for prolonged time leads to permanent adverse health effect like dental, skeletal and soft tissue fluorosis on human and animals. (Khajeian, 2013) (Ramavandi *et al.,* 2017)

Hence, fluoride has been classified as a notable pollutant by the united states environmental protection agency (USEPA, 1986). Consequently, the World Health Organization (WHO) has restricted the acceptable fluoride concentration limits in drinking water between 0.5 and 1.5 mg/l. (WHO, 1994). The Bureau of Indian standards, (BIS (IS-10500) has prescribed desirable limits and permissible limits of fluoride in drinking water as 1.0 and 1.5 mg/l respectively. (BIS, 1991). Therefore, it is essential to protect the lives of humans and animals by removal of fluoride ions from drinking water before intake in the body. In the present context several reports are available in literature for the removal of toxic materials, especially fluoride from various parts of the world including India.

Several potential techniques have been implemented for removing or reducing fluoride concentration such as ion exchange, precipitation,

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adsorption, electrolysis, nanofiltration and reverse osmosis. (Bhatnagar *et al.,* 2011) (Kumar *et al.,* 2015). Some of these are restricted due to their high energy consumption and high volume of slug production, therefore, there is an urgent need to provide some cost-effective alternatives. Among the various methods, the adsorption process is proven to be the most efficient and beneficial technique which is used most commonly due to its simplicity, high efficiency and low cost for treating fluoride and other toxic ions (Saka *et al.,* 2012). Many efforts have been made on eliminating groundwater toxicants by adsorption methods using various types of sorbents. Ceramic adsorbents were prepared by mixing kanuma mud with zeolite, starch and ferrous sulphate for removal of fluoride from aqueous solution. (Mondal *et al.,*2012). Removal of fluoride using cationic saw dust derivatives were reported for 80% percent of toxicant by achieving equilibrium less than 30 min. (Prasad Rao *et al.,* 2014). Feasible optimum conditions were employed for defluoridation of groundwater using brick powder as effective and low-cost adsorbent was studied at different parameters (Zhang *et al.,* 2010). Dharmidirakuamr *et al.* (2012) reported for the feasibility of basic dye rhodamine-B from aqueous solution natural adsorbent perlite.

Activated carbon has been considered as one of the most common and widely studied low-cost adsorbent for sorption of variety of material such as metal ions, dyes, phenols, organic and bio-organic compounds and therefore, used as an excellent agents for removal of pollutants from wastewater by adsorption due to its high porosity, large surface area, thermal stability and versatile surface chemistry (Bansal and Goyal, 2005) (Yadav *et al.,* 2006) (Wang *et al.,* 2015). Since the operational costs of adsorption are mainly determined by the price of an adsorbent, there is growing interest in looking for alternative precursors for producing some new low-cost active carbons.

Bio-adsorbents have come up as one of the promising scaffolds for the adsorption process which can eliminates different type of toxic organic and inorganic pollutants present in industrial waste and groundwater. Low-cost bio sorbent could be obtained from numerous raw materials such as industrial and agricultural waste which are easily available in large abundance in local field areas (Ramavandi, 2017). In recent years preparation and application of activated carbon from bio-material have been paid more and more attention.

Natural biopolymer like chitosan has been extensively studied and applied for industrial waste treatments. Sudha *et al.* (2017) prepared doubly grafted chitosan with maleic anhydride and ethylene dimathacrylate for adsorption of Chromium and Copper from aqueous solutions. Cost effectiveness and progressively adsorption isotherms were reported for further use of bio adsorbents for industrial effluents treatment on large scale (Sudha *et al.,* 2017). Chemically modified cationic starch derivatives have been reported as an efficient scaffold for removing fluoride from groundwater with no waste disposal problem. (Choudhary *et al.,* 2018)

Some biosorbents such as marine food waste, leaf biomass, bone char, agricultural husk, activated alumina, activated charcoal have been demonstrated as effective agents for eliminating fluoride. Activated carbon prepared from banana peel and coffee husk was undertaken for fluoride removal efficiency and adsorption capacities of the materials used for the purpose. (Hussen, 2014). A large number fo research groups have been focused on finding new economic bio sorbents with high adsorption capacities along with their easy and abundant availability. Therefore, the efforts are still underway in finding out such materials that have an adequate sorption capacity.

Prosopis cineraria, also known as *Khejri* in Rajasthan, is a species of the flowering tree that belongs to *Leguminosae* family. It is native to arid portions of western Asia and the Indian subcontinent, including Afghanistan, Bahrain, Iran, India, Oman, Pakistan, Saudi Arabia, the United Arab Emirates and Yemen. In India, it is found mainly in Rajasthan, Haryana, Gujrat, western Uttar Pradesh and in some drier parts of deccan (Maheshwari *et al.,* 2013). The waste leaves of this tree could be a suitable tool for the elimination of toxic ions. Biowaste from this tree have been used to remove pollutants such as malachite green (Garg *et al.,* 2004), cadmium (Rao *et al.,* 2010) and organic dye and eosin B (Mehmood *et al.,* 2015).

Present study is reported for the application and evaluating optimized sorption conditions for *P. Cineraria Leaves* (PCL) for reducing the toxic levels of fluoride ions from aqueous solution. Modified bio waste was used to remove fluoride from ten groundwater samples collected from Gadra road region in Barmer district of thar desert, Rajasthan. This biomaterial is easily available in large abundance in the field under taken for the study.

Operational parameters such as initial concentration of fluoride ion, adsorbent dosage and contact time and optimum pH were evaluated. The equilibrium adsorption data were evaluated by Freundlich and Langmuir isotherm models.

MATERIALS AND METHODS

Chemicals

All the chemicals used were of analytical grade and were used directly as received. A standard stock solution of fluoride ion was prepared by making 100 mg/L fluoride by dissolving 0.221 g of anhydrous NaF into 1000 ml of distilled water at room temperature. Fluoride solutions of varied concentration were prepared by appropriate dilution of stock solution. All the experiment was carried out in 250 ml conical flask with a total of 100 ml experimental solution at room temperature. These flasks with adsorbent material and fluoride solution were stirrer for studying the various parameters. The adsorption process was subjected to varying doses of adsorbent, initial fluoride concentration, pH and contact time.

Preparation of Bio-sorbent

Prosopis cineraria leaves (PCL) for the proposed work were collected from areas nearby Gadra road of Thar Desert. Then the samples were transferred to the environmental analytical laboratory and washed with normal tap water and then rinsed with deionized water several times to remove dust and other impurities and were kept in porcelain trey to dry them in sunlight for 72 hrs. After this, the leaves samples were crushed and sieved to obtain mesh size less than 0.6 mm. Two different types of carbonized Cineraria leaves activated carbon (PCAC) were prepared and compared for optimal adsorption.

First type (only carbonization): a certain amount of PCL powder was placed in a crucible, covered with a lid and then carbonized in the electric furnace at a temperature at 600 ^{0} for 2 h. the heating rate of furnace was set at 10 ^{0}/minute. After the process, the product was cooled naturally at room temperature then stored in a sealed quartz sample bottle for further use. The obtained carbonized sample were denoted as PCAC.

Second type (Pre activation before carbonization**)**: the crushed leaves powder was mixed with H_3PO_4 in the ratio of 1:1.5 at room temperature for 4 hrs.

Phosphoric acid was used to activate the adsorbent and to enhance the adsorbent capacity (Zuo *et al.*, 2009). Certain amount of obtained material after activation were placed in crucible covered with a lid is carbonized in electric furnace at temperature 600 ^{0} for 2 h. Obtained samples were washed with 0.1 M sodium bicarbonate solution to modify pH between 6 to 8. Then dried the sample in an oven at 110-120 ^{0} for 1 h. After that the material was allowed to cool at room temperature in desiccator. The PCAC sample after carbonization at 600 ° was marked as PA-PCAC.

Fluoride adsorption Experiments

Both the prepared bio sorbents were exposed for the fluoride adsorption process. The effect of sorbent doses (1, 2, 4, 6 and 8 g), contact times (5,10,20, 30, 60,90 and 120 min), pH (ranged from 2-12) and varying initial fluoride concentrations (4, 8, 12, 16, 20 mg/l) were investigated. For each batch experiment known concentration of 100 ml of fluoride solution was taken in 250 ml conical flask with known amount of adsorbent and assessed for adsorption process at preset contact time at room temperature. This solution is then stirred continuously using a magnetic stirrer to achieve adsorption equilibrium. After the equilibrium, all the solutions were taken out from the flask and filtered through Whatman filter and concentration of residual fluoride was determined. The removal efficiency (%) and adsorption capacity (mg/g) for a particular experiment were determined using the following equations No 1 and 2.

$$\text{Removal efficiency (\%)} = \frac{|c_i - c_t|}{c_i} \times 100 \quad\text{.........(1)}$$

$$\text{Adsorption capacity (mg/g)} = \frac{|c_i - c_t|}{m} \times V \quad\text{........(2)}$$

Where C_i is initial fluoridation concentration (mg/l), C_t is residual fluoride concentration (mg/l) at time t (min), m is mass (gm) of adsorbent and V is the volume of solution (L) used in the batch.

RESULTS AND DISCUSSION

Results were analyzed for optimization of parameters by varying one parameter with keeping other parameters constant is the best way to make a particular parameter at its best. The effect of major parameters like adsorbent dose, contact time, pH and initial fluoride concentrations were optimized.

Effect of adsorbent doses

Fluoride removal experiment was conducted at different adsorbent doses ranging from 1 to 8 g/100 ml of prepared adsorbents for fixed fluoride concentration at 5 mg/l keeping solution pH at 7±0.4 and contact time for 90 min at room temperature. The result was presented in terms of percentage removal and adsorption capacity in Fig. 1. The removal of fluoride increases from 58.2 to 84.9 % and 65.5 to 88.1 % for PCAC and PA-PCAC respectively as the adsorbent dose increases. It was seen in Figure 1 that initially percentage removal increases remarkably but after a certain dose of adsorbent there was no significant change in removal percentage which is due to overlapping of the active site hence reducing the net surface area. Thus, as from experimental results the optimize dose for efficient removal of fluoride by prepared adsorbent is 6.5 ± 0.5 g/l. On the other hand,
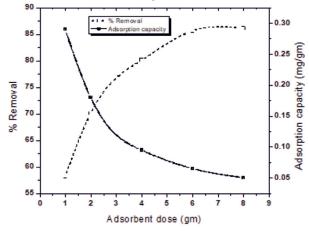
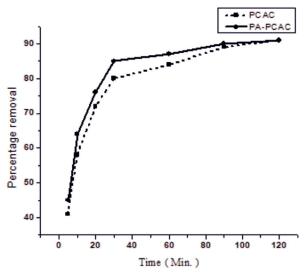adsorption capacity decreases with an increase in adsorbent dose due to possibility of aggregation of adsorbent at higher concentration therefore decreasing the area of surface contact between adsorbent and adsorbate. In fact, with increase in adsorbent dose, more adsorbent active site remains unsaturated during the process, thus the capacity may decrease. This is accordance with previous resulted reported in the literature. (Ghoreyshi *et al.*, 2012).

Effect of contact time

The percentage removal of fluoride at different times is shown in Figure 2. It is shown that initially, % removal increases as contact time increases but after some time it gradually approached to almost constant indicating to the attainment of adsorption equilibrium. At equilibrium, the curve appears nearly asymptotic with the time axis. In the present study, the equilibrium time was obtained at 80 ± 5 min with 88% removal of fluoride. The constant rate of fluoride removal at equilibrium may be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. After some time, the fluoride uptake rate decreases significantly due to decrease in the number of vacant adsorbent sites and the formation of possible monolayer of fluoride ions on the outer surface (Raza *et al.*, 2020).
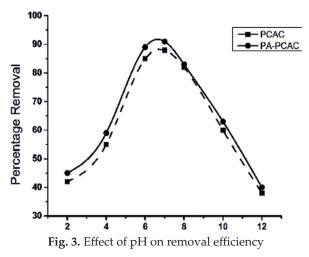
Effect of pH

The effect of pH on removal of fluoride was studied in the pH range from 2.0 to 12.0 and results are

Fig. 1a. Effect of sorbent dose of PCAC on removal eficiency and capacity

Fig. 1b. Effect of sorbent dose of PA-PCAC on removal eficiency and capacity

Fig. 2. Effect of contact time on removal efficiency by both bio sorbents

shown in Figure 3. Maximum fluoride adsorption was found at pH range between 6.0 to 8.0 with percentage removal of 84– 80 %, 89- 83 % for PCAC and PA-PCAC respectively. Efficiency was found to be decreasing as pH decreases below 6.0 or above 8.0. This is because in acidic medium there is formation of weakly ionised hydrofluoric acid which reduces the availability of free fluoride ions and in alkaline medium presence of OH- compete with F- ions for adsorption. The reported result was found in comparison with fluoride adsorption by rare earth oxides (Raichur, 2001).
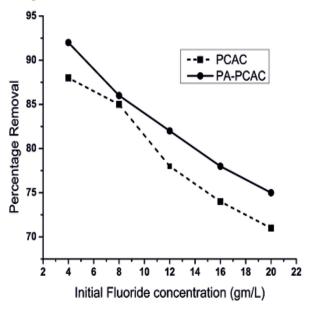

Fig. 3. Effect of pH on removal efficiency

Effect of initial fluoride concentration

The removal efficiency for the adsorbents were decreasing with an increase in fluoride concentration. It was observed that there is significant decrease in removal efficiency when the initial fluoride concentration is equal to or less than 8 mg/l and if fluoride concentration is raised above from 10 mg/l to 20 mg/l this removal efficiency decreased sharply. This behaviour is illustrated in Figure 4. Higher efficiency at lower fluoride concentration may be due to higher ratio of active sites to adsorbate concentration. The reason for the sharp decrease in removal efficiency with the increase in initial fluoride concentration is the lack of sufficient surface area to accommodate more fluoride ions available in the solution (Prasad, 2009).

Adsorption study on collected ground water samples

Groundwater samples were collected from ten different sites nearby Gadra road village and all the samples were analyzed for fluoride concentration using ion selective electrodes in the laboratory. The sites chosen for the sampling are located

approximately 80 km from district headquarter of Barmer, Rajasthan and situated nearly at Indo-Pak Border. The residents of these area are dependent only on natural sources for drinking water as there is no public water system provided by the government till date. The ground water is the only source for this purpose there. The major sources for ground water are tube-wells or local name 'Beri'. Samples were collected from these tube-well of

Fig. 4. Effect of initial Fluoride concentrations on removal efficiency by the both sorbents

average depth of 800± 200 feet. The concentrations of fluoride ion almost in all the water samples collected are observed to be higher than the permissible level. Prepared sorbents were subjected for fluoride removal efficiency for collected samples under specified optimized conditions. These results are shown in Table 1.

Adsorption isotherm

The distribution of sorbate between solid and solution interface at equilibrium has been described by adsorption isotherms, which demonstrates mathematical explication of adsorption behaviour of a given adsorbate species based on surface activity of adsorbent and possible interaction between species. Adsorption experimental data are usually subjected to both the adsorption isotherms such as Langmuir and Freundlich isotherms. The results of the adsorption experiment data were fitted to Freundlich and Langmuir isotherm models for the description of the adsorption process.

Freundlich isotherm

Freundlich isotherm model applies to adsorption processes on heterogonous surfaces with the interaction between the adsorbed molecules and it is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centres of the adsorbent. (Freundlich, 1928) Linear forms of Freundlich equation is follows as equation No. 3

$$log q_e = log K_f + \frac{1}{n} log C_e \ldots\ldots\ldots(3)$$

Where q_e is the amount of fluoride adsorbed by per unit mass of adsorbent (mg/g). C_e is residual adsorbate concentration (mg/l) at equilibrium in solution after adsorption and K_f and n are Freundlich constants which indicate the adsorption capacity (mg/g) and adsorption intensity respectively. The value of adsorption intensity (n) more than 1 (n > 1) indicates about favourable condition for adsorption. (Shahabuddin, 2009). Figure 5(a) and 5(b) shows the experimental equilibrium isotherm through a linear graph plotted between log q_e against log C_e which demonstrates that adsorption behaviour is obeying Freundlich model. The value of Freundlich constants K_f and $1/n$ are determined by intercept and slope respectively and are depicted in Table 2. The values of n (2.43 and 1.51 for PCAC and PA-PCAC respectively) for both the bio sorbents were found to be more than one indicates for physical adsorption process. The situation of n >1 is most common and may be due to

distribution of surface sites or any factor that causes a decrease in adsorbent- adsorbate interaction due to decrease in bond energy with increase in surface density (Reed, 1993).

Langmuir isotherm

The Langmuir isotherm model is based on the assumption that there is a finite number of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbed molecules. (Langmuir, 1918). Langmuir adsorption which was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the adsorptive capacity of various adsorbents (Elmorsi, 2011).
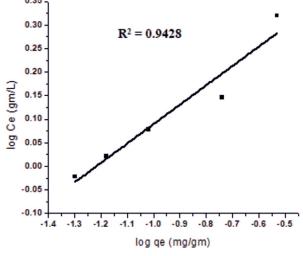
Langmuir isotherm can be represented as

Fig. 5a. Freundlich isotherm for PCAC sorbent

Table 1. Fluoride removal from groundwater samples using adsorbents prepared from PC leaves

Sampling Sites	Concentration before treatment (Mg/l) Average concentration ± Sd ± Sd	Concentration of fluoride after treatment with adsorbents			
		PCAC		PA-PCAC	
		Average concentration	% removal	average concentration ± Sd	% removal
Padhariya	6.1±0.03	0.67±0.03	89.0	0.62±0.06	89.9
Lakhe ka Tala	3.5±0.03	0.47±0.03	86.5	0.41±0.09	88.2
Bhojariya	2.9±0.03	0.33±0.07	88.3	0.32±0.09	89.1
Chandaniyan ka Par	2.1± 0.01	0.24±0.07	88.1	0.26±0.02	87.6
Bane ki Basti	2.8±0.01	0.30±0.03	89.1	0.34±0.03	88.0
Chandi ka Par	3.0±0.02	0.37±0.01	87.8	0.35±0.08	88.5
Bindu sinhani	2.0±0.03	0.22±0.03	89.0	0.30±0.06	89.9
Bukar	5.3±0.01	0.74±0.05	86.0	1.05±0.05	84.9
Lakriyali	1.8±0.05	0.25±0.20	86.2	0.22±0.11	87.3
Bheende ka par	3.9±0.09	0.66±0.09	83.0	0.64±0.02	83.6

following linear form equation no. 4

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \qquad .. (4)$$

q_m and K_L are Langmuir constants which represent maximum adsorption capacity (mg/gm) and binding affinity of adsorbent (l/mg) respectively. A plot of $1/C_e$ verses $1/q_e$ should be obtained as a straight line with a slope of $1/q_m K_L$ ans intercept equal to $1/q_m$.

The linear plot of $1/q_e$ against unadsorbed fluoride concentration $1/C_e$ {Figure 6(a) and 6(b)} demonstrates that the adsorption is obeying the Langmuir isotherm model. The Langmuir constants q_m (mg/g) and K_L were determined from the intercept and slope respectively from the graph and represented in Table 2.

Characteristics of Langmuir isotherm can be expressed in term of a dimensionless constant known as separation factor or equilibrium parameter R_L which can be represented as the following equation no. (5)

$$R_L = \frac{1}{1 + K_L C_o} \qquad .. (5)$$

Where C_o is initial fluoride concentration (mg/L) and K_L (L/mg) is Langmuir constant. The R_L value indicate the type of isotherm to be irreversible
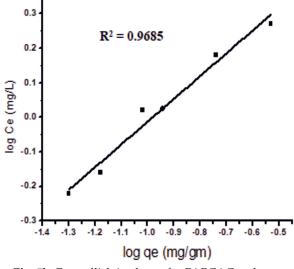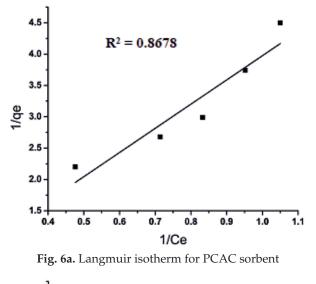
($R_L=0$), favourable ($0<R_L<1$), linear ($R_L=1$) and unfavourable ($R_L>1$). (Hall *et al.*, 1966). The value of $R_L< 0$ (Table 2) indicates favourable sorption of fluoride onto active carbon prepared from PCL.

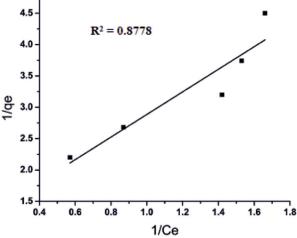**Fig. 6a.** Langmuir isotherm for PCAC sorbent

Fig. 6b. Langmuir isotherm for PA-PCAC sorbent

The linear equations for both isotherms were applied to correlate the amount of fluoride adsorbed per unit mass of the adsorbent. All the adsorption isotherm parameters obtained from these models and the values of the correlation coefficient (R^2) are depicted in Table 2.

Fig. 5b. Freundlich isotherm for PAPCAC sorbent

Table 2. Adsorption parameters for fluoride by PCAC and PA-PCAC

Adsorbents type	Freundlich parameters			Langmuir parameters			
	n	K_F	R^2	$q_{m\ (Mg/g)}$	$K_{L\ (L/mg)}$	R_L	R^2
PCAC	2.43	3.16	0.9428	47.61	0.052	0.793	0.8678
PA-PCAC	1.51	4.42	0.9685	61.29	0.067	0.747	0.8778

Initial [F⁻] = 5.0 mg/l; Adsorbent dose = 6.0 g; pH = 7.0; contact time = 90 min.

The Langmuir constants q_m and K_L were determined from a linear curve plotted between $1/qe$ verses $1/Ce$. The R_L values for the adsorbents PCAC and PA-PCAC and are 0.793 and 0.747 respectively, which implies favourable conditions for adsorption. For both the isotherms linear plot were obtained and through the degree of linearity for Freundlich isotherm plots is higher (0.9428 and 0.9685 for PCAC and PA-PCAC respectively) than that of Langmuir isotherm plots (0.8678 and 0.8778 respectively) indicates that the data were more in favour of Freundlich isotherm as compared to Langmuir isotherm. However, both the isotherms are applicable for the presented adsorption process.

CONCLUSION

The present investigation showed considerable potential for the removal of fluoride from aqueous solution by biosorbent obtained from activated carbon of *Prosopis Cineraria leaves*. The adsorption was found to depend on various parameters employed in the present study. The experimental results showed that percentage removal increased with an increase in contact time and adsorbent doses while decrease with an increase in initial fluoride concentration. Whereas the adsorption capacity decreases with an increase in adsorbent dose. At the optimum condition of pH and contact time bio sorbent prepared from PCL exhibited maximum removal efficiency of 85 and 88 % for PCAC and PA-PCAC respectively for 5 mg/l of initial concentration of fluoride, reveals that impregnated leaves powder found to be more efficient than non-impregnated leaves powder. On the basis of results obtained and fitted in both the isotherm models, it was observed that adsorption follows Freundlich isotherm as compared to Langmuir isotherms.

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Conflict of interest

The authors declare that they have no conflicts of interest.

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