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Bioadsorption of Fluoride by *Ficusreligiosa* (Peepal Leaf Powder): Optimization of process Parameters and Equilibrium study

Shubha Dwivedi[1,2], Prasenjit Mondal[3] and Chandrajit Balomajumder[3]
[1]Uttarakhand Technical University, Dehradun, INDIA
[2]Department of Biotechnology, S.D. College of Engineering and Technology, Muzaffarnagar, UP, INDIA
[3]Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, INDIA

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Abstract

Presentinvestigation focused on the bioadsorption of fluoride from aqueous solution by Ficusreligiosa (peepal) leaves. Removal of fluoride has been investigated as a function of pH, bioadsorbent dose, temperature, time and equilibrium initial fluoride ion concentration. Batch study exposed that the bioadsorption of fluoride on Ficusreligiosa (peepal) leaves were strongly pH dependent, and maximum fluoride removal was found to occur at equilibrium pH of 7. Optimum adsorbent dose, temperature, time and initial concentration were found 10 g/L, 30 ^{0}C, 45 min and 20 ppm respectively. Characterization of peepal leaves, before and after adsorption were studied by Scanning Electron Micrograph to get a well understanding into the mechanism of adsorption.

Keywords: Bioadsorption, fluoride, *Ficusreligiosa.*

Introduction

Endurance of life on the earth only is conceivable because of water. Near about 97% of earth's surface is covered by water. It is very essential source for maintaining the life. There is a large amount of water present on the earth and the whole amount of water reserves divided into two parts, marine water which covers the 97.4% of total water reserves and fresh water which cover only 2.6%. But from the past few years, it seems in the reduction in water quality because of urbanization, ever growing population, and unskilled utilization of water resources. But from the last few decades, these water resources get polluted by various natural and anthropogenic contaminants like heavy metals, fluoride, arsenic, lead, mercury etc. Among these, fluoride contamination of water has now become a major issue in most of the part of the world because of its toxic effects. The prominent fact about fluoride is that it affects the majority of children who are living in the contaminated areas. In very little quantity, fluoride is very important component for mineralizing the bones and formation of the tooth enamel[1]. Around one million people in India are affected by endemic fluorosis[1,2]. Maximum permissible limit of fluoride in drinking water has been set as 1.5 mg/l by many regulatory authorities like WHO, US EPA, CPCB etc. Defluoridation of drinking water is the only feasible option to root out the problem of excessive fluoride in from water, where alternate source is not available. There are many methods exist to remove fluoride from contaminated water i.e. adsorption, Ion exchange, electrodialysis, coagulation/ precipitation, Donnan dialysis, reverse osmosis, nanofiltration and ultrafiltration have been investigated[3-15]. All these methods have their inherent merits and demerits such as less efficiency, sensitive operating conditions, production of secondary sludge in application. Amongst the above processes, adsorption is a simple and attractive method for the removal of metal from the effluents due to its high efficiency, easy handling and economic feasibility. Further, agro based adsorbents are getting more consideration now a days due to their abundant availability and low cost. Some literatures are available on the removal of fluoride from water using various agro based adsorbents like mosambi fruit peel powder[16], *Phyllanthus emblica*[17],*Citrus limonum*(lemon) leaf[18], rice husk ash[19], neem leaf, peepal leaf , khair leaf[20], tamarind fruit shell[21] etc. In most of these literatures the concentration of fluoride is in between (1.5-15 mg/l). However, industrial wastewater normally contains higher fluoride concentration[22] and there is very few literature on the removal of fluoride from water containing fluoride at higher concentration i.e. 20 ppm. Therefore, in this work the potential of peepal leaf powder agro- based biomass for the removal of fluoride from water has been explored. The characterization of peepal leaf powder has been done by using scanning electron microscope (SEM). Experimental studies on fluoride removal have been done in batch reactor configuration. The effects of solution pH, adsorbent dose, temperature, time and initial concentration on the removal of fluoride have been studied and equilibrium parameters for the initial fluoride concentrationhave been estimated.

Material and Methods

All chemicals used in the present study were purchased from LobaChemie, Fisher Scientific and of analytical grade. Stock solution (100 ppm) of fluoride was prepared by Milli-Q water

(BioPAK Polisher, L. No. F2NA57203) by dissolving 221 mg anhydrous sodium fluoride in one litre water[23].

Pretreatment of bio-adsorbent: Fresh leaves chosen based on their crude fiber content and tress were obtained from peepal tree. The fresh leaves were sun-dried for 3–4 days, put in a cotton jute bag and first crushed manually into smaller particle size and then sieved into desired particle size.Physical properties and ultimate analysis of the untreated peepal leaf powder are shown in table 1.

Procedure: Batch sorption experiments were performed adopting independent flask method. In this method, each independent flask containing the adsorbent and fluoride mixture in order to get accurate results. A series of 100 ml Stoppard flask with 10 g/L of bioadsorbent were taken and 50 ml of solution containing fluoride concentration of 20 ppm were added and the adsorption mixture was agitated for a predetermined time period using orbital shaker temperature: 29 $\pm 1^0$C; agitation: 125 rpm; bioadsorbent mass: 10 g/L, pH 7. After completing the agitation time, batches were used for the centrifugation. After centrifugation, 10 ml supernatant of each batch was taken out for further analysis[21]. To get the optimum process conditions for bioadsorbent the effect of process variable such as pH, adsorbent dose, temperature, time and initial fluoride concentration on the removal of fluoride was studied. The conditions used for these experiments are shown through table 2.

In each case, after the adsorption the solutions were filtered through Whatman no 42 filter paper[24] and the filtrate was analyzed through SPADNS [23] photometric method, at 570nm using the UV–Vis spectrophotometer (UV–210 A, Shimandzu, Australia) to determine fluoride concentration.

% adsorption (A) of fluoride was calculated as using following formula:

$$\% \text{ A} = \frac{(\text{Ci} - \text{Cf})\text{X } 100}{\text{Ci}}$$

Where C_i and C_f are the initial and residual concentration at equilibrium (ppm).

Results and Discussion

Removal of fluoride species by peepal leaf powder has been studied in the present investigation and the effects of various process parameters such as pH, adsorbent dose, time, temperature and initial fluoride concentration are discussed as follows:

Effect of pH: Effects of solution pH on the removal of fluoride for adsorbent are shown in figure 1. From figure 1, it seems that at the lower pH, the % removals of fluoride for peepal leaf powder are less, which increase gradually with the increase in solution pH, reach maximum at around pH 7 and decrease thereafter. At pH 7, % removals of fluoride for peepal leaf powder is 74.

Table-1
Physical properties and ultimate analysis of thepeepal leaf powder

Elemental analysis peepal leaf powder					Physical properties of peepal leaf powder		
C	H	N	S	O	M (%)	Ash (%)	Particle size (µm)
43.15	8.92	2.98	0.00	59.39	9.8	13.1	<196

Table-2
Ranges of operating parameters for pH, adsorbent dose, temperature, time and initial fluoride concentration for the removal of fluoride

Objective of experiment	Values of variable parameters	Values of fixed parameters for verifying optimum conditions
To study the effect of pH on fluoride removal	Solution pH: 2,3,4,5,6,7,8,9	AD: 10g/L; IFC: 20 ppm; Temp.: 30^0C;Time: 45 min.
To study the effect of time on fluoride removal	Time: 5, 10, 15, 20, 25, 30, 45, 60, 90, 120 min.	AD:.10g/L ; IFC:20 ppm; Temp.: 30^0 C ; Solution pH:7
To study the effect of adsorbent dose on fluoride removal	AD: 2,4,6,8,10, 12, 16, 20, 30, 40 g/L.	IFC: 20ppm ; Temp.: 30^0 C ; time: 45 min; Solution pH 7
To study the effect of temperature on fluoride removal	Temp: 20, 25,30,35,40 ^{0}C	AD: 10g/L; IFC: 20ppm; Time.: 45 min; Solution pH:7
To study the effect of initial fluoride ion concentration on fluoride removal	IFC: 1, 5, 10, 15, 20 ppm	AD:10g/L; Time.: 45 min; Solution pH:7; Temp: 30 ^{0}C

AD: Adsorbent dose, IFC: Initial fluoride concentration.

The solution pH shows significant effects on the removal of adsorbates from water because the variation of solution pH significantly alters the surface charge of the adsorbent as well as solution phase chemistry of the adsorbate. Fluoride can be adsorbed on the surface of adsorbents by the following reactions[21].

$HF \leftrightarrow H^+ + F^-$ (1)
$\equiv POH + H^+ \leftrightarrow POH_2^+$ (2)
$\equiv POH + OH^- \leftrightarrow PO^- + H_2O$ (3)
$\equiv POH_2^+ + F^- \leftrightarrow PF + H_2O$ (4)
$\equiv POH + F^- \leftrightarrow PF + OH^-$ (5)

Where POH, POH_2^+ and PO^- are the neutral, protonated and deprotonated sites on peepal leaf powder and PF is the active site–fluoride complex.

At lower pH, the surface of the peepal leaf powder adsorbent is predominantly positive since more protonation takes place with the adsorbent sites through equation 2 and the fluoride species exist predominantly as HF (pKa = 3.2), which is weakly ionized, thus the removal of fluoride is less[25]. With increase in solution pH the dissociation of the HF increases and the positive charge density of peepal leaf powder adsorbent also gradually decreases. However, up to pH 7 it remains predominantly positively charged with some neutral sites[21], which results maximum removal of fluoride at pH 7. However, above pH 7 the increase in solution pH converts the surface of the peepal leaf powder adsorbent as predominantly negatively charged through equation 3, where fluoride also predominantly exists as negatively charged fluoride ion. Thus, the repulsive forces between the peepal leaf powder adsorbent and the fluoride reduces chemisorption of fluoride at pH greater than 7 as a result the % removal of fluoride decreases. Similar observation on the fluoride adsorption by ATFS and MTFS has been reported by V. Shivashankar et.al.[21].

From SEM micrographs of peepal leaf powder adsorbents before and after adsorption as shown in figure 2(a-b) it is evident that active sites of adsorbents are covered due to the adsorption of fluoride on it.

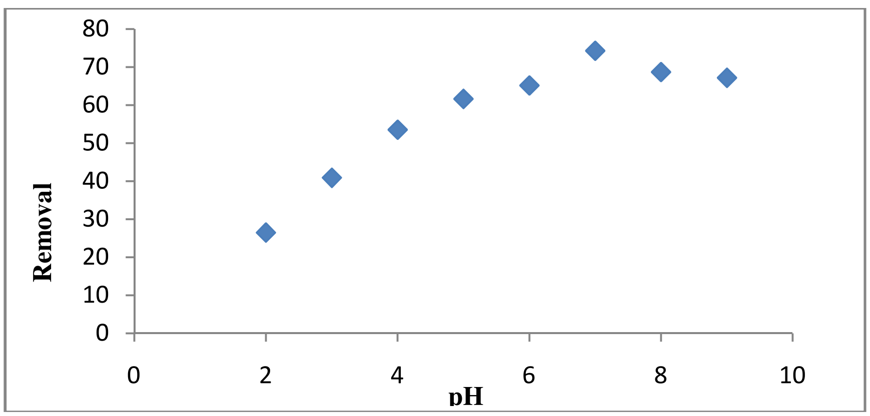

Figure-1
Effect of pH on the removal of fluoride species by peepal leaf powder Process conditions: temp: 30^{0}C, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20ppm, rpm: 125

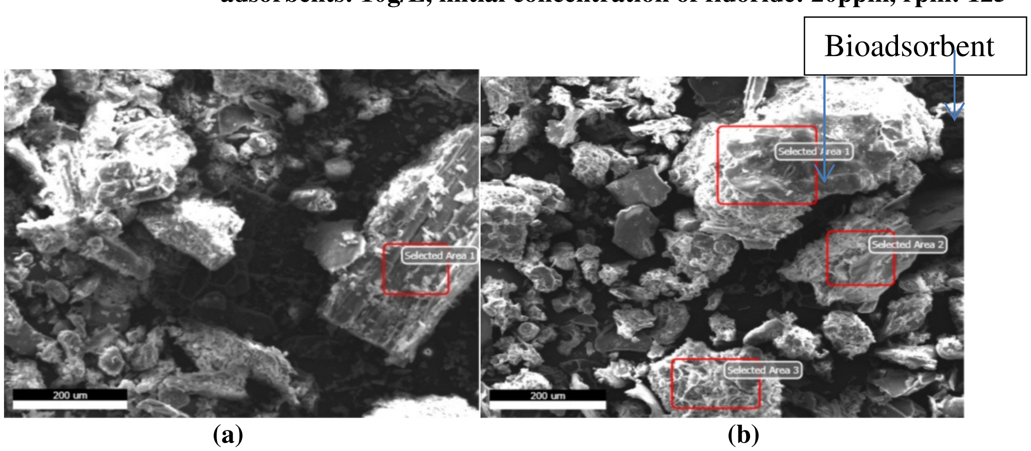

Figure-2
Scanning Electron Micrograph of peepal leaf powder; (a) Peepal leaf powder before adsorption, (b) Peepal leaf powder after adsorption

Effect of time: The effect of contact time on the removal of fluoride from synthetic water is shown in figure 3. From figure 3 it is evident that with the increase in contact time the % removal of fluoride increases very fast initially however, above 45 min of contact time the adsorption rate virtually remains constant. At the contact time of 45 min the % removal of fluoride is around 74 %.

Effect of adsorbent dose: The effect of adsorbent dose on the % removal for fluoride from synthetic water is shown in figure 4. From figure 4 it is evident that the % removal of fluoride increases initially with increase in adsorbent dosage and around 74.0 % of fluoride is removed at the adsorbent dose of 10 g/l by untreated adsorbent. However, above the adsorbent dose of 10 g/l the increase in adsorbent dose can not improve the % removal of fluoride noticeably. Hence, the optimum removal of fluoride species can be obtained by using 10 g/l. Initially the increase in % removal with increase in adsorbent dose is very high as the removal of adsorbate depends on the number of available active sites, which increases with increase in adsorbent dose.

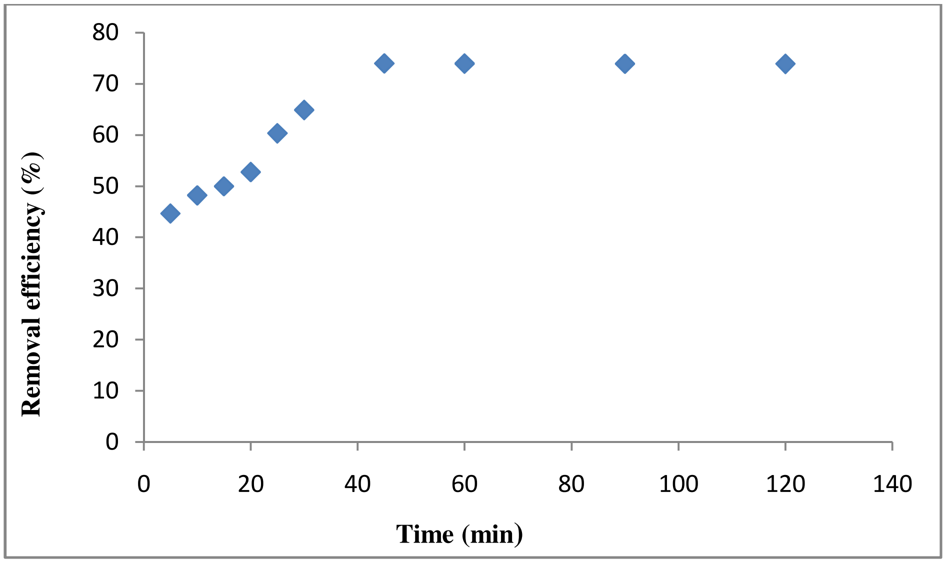

Figure-3

Effect of time on the removal of fluoride species by peepal leaf powder (Process conditions: temp: 30 ^{0}C, pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20ppm, rpm: 125)

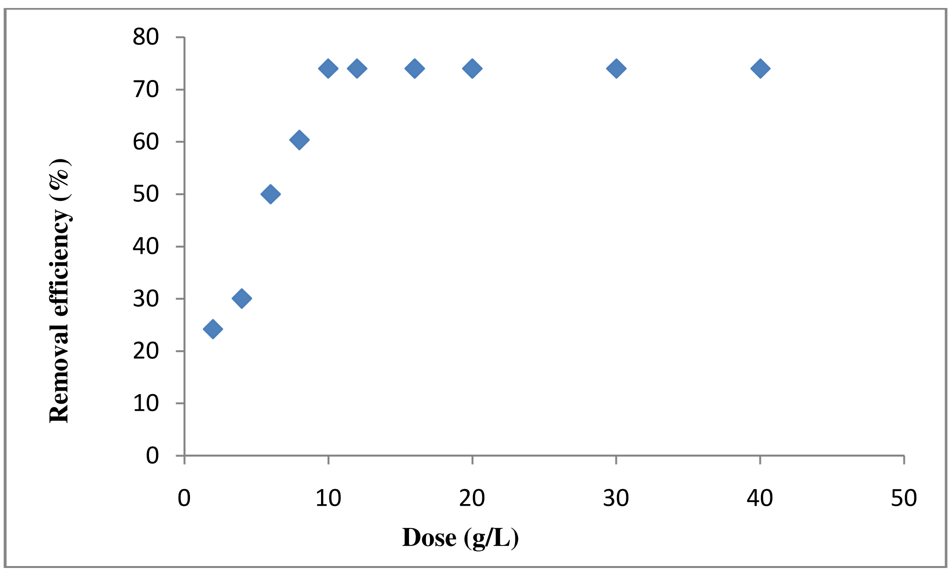

Figure-4

Effect of adsorbent dose on the removal of fluoride species by peepal leaf powder (Process conditions: temp: 30^{0}C, pH: 7, initial concentration of fluoride: 20ppm, rpm: 125)

Effect of temperature: Effect of temperature on the removal of fluoride is shown in figure 5. From figure 5 it is noteworthy that with the increase in temperature percentage removal of fluoride increases. At lower temperature (<30^{o}C) the incraese in % removal of fluoride with the increase in temperature is more with respect to the corresponding values at higher temperature (> 30 ^{o}C). The increase in sorption with temperature may be attributed to either increase in the number of active sites available for sorption on the adsorbent or due to the decrease in the boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of absorbate in the boundary layer decreased[26](Venkata Mohan et al. 2007).

Effect of initial concentration: The specific uptake of fluoride by adsorbent for the removal of fluoride from water is shown in figure 6. From figure 6 it is clear that the specific uptake increases from 0.09 mg/g to 1.48 mg/g with the increase in initial fluoride concentration from 1 mg/L to 20 mg/L. With increase in initial concentration of fluoride the driving force for transport of fluoride from the bulk to the surface of adsorbent increases, which results more adsorption of fluoride per unit mass of adsorbent. It is also evident that the fluoride concentration at the treated water is around 0.7 mg/L, which is below the permissible limit (1.5 ppm) of fluoride in ground water when the initial concentration of fluoride is 5 mg/L. It seems that the present adsorbent can be used for the treatment of fluoride contaminated groundwater since fluoride concentration in ground water is normally < 5 mg/L.

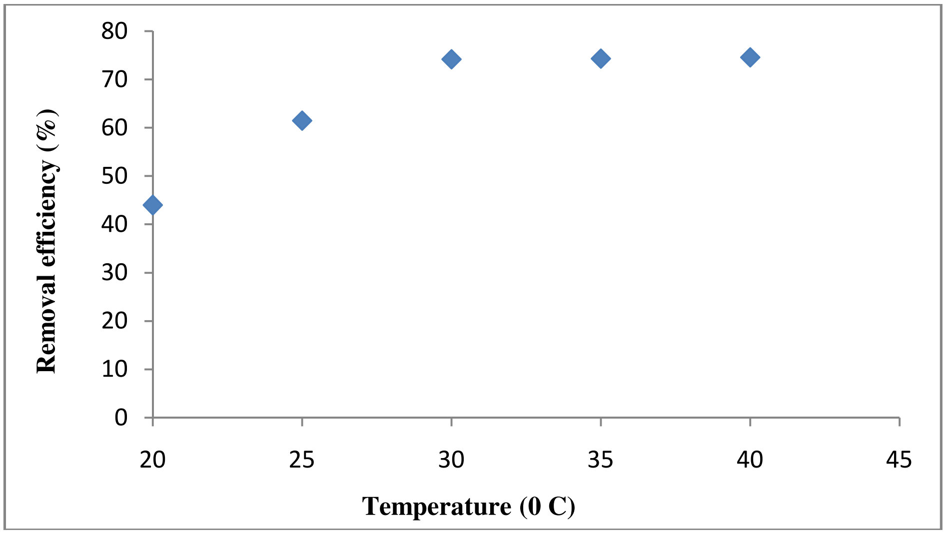

Figure-5

Effect of temperature on the removal of fluoride species by peepal leaf powder (Process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20ppm, rpm: 125)

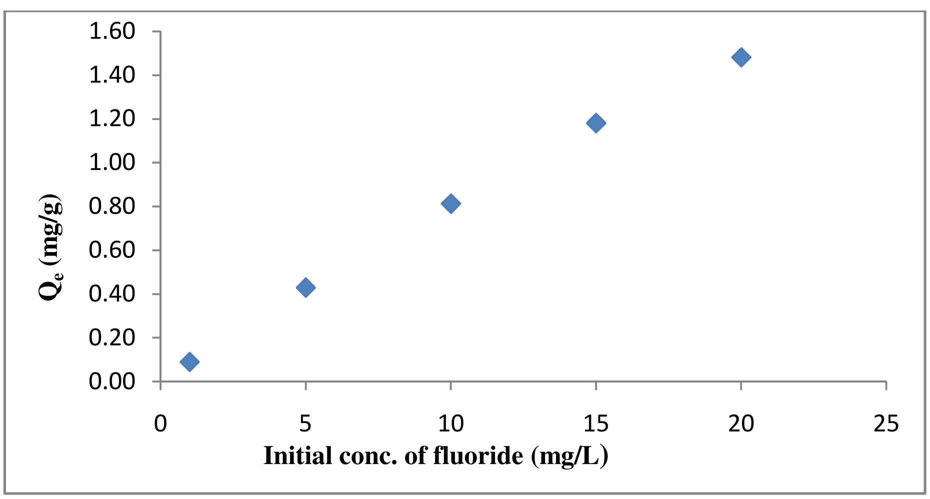

Figure-6

Specific uptake of fluoride species by peepal leaf powder (Process conditions: temp: 30 ^{0}C, pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 30 min)

Optimization of process parameters: Process parameters for the optimum bioadsorption of fluoride from synthetic industrial waste water using peepal leaf powder; have been determined by analyzing the observations of Section 3.1 to 3.5 and are reported in table 3.

Equilibrium study for fluoride removal: To find out a suitable model equation for predicting equilibrium adsorption of fluoride from water Freundlich, Langmuir and Temkin isotherm models have been tested[21]. To find out the isotherm constants the nonlinear models were linearized as described in table 4.

In the present work, the R_L values calculated in the studied range of fluoride concentration are found to be 0.13 which falls in the range of 0–1, which suggests the favourable sorption of fluoride onto the studied peepal leaf powder, under the conditions used for the experiments. For peepal leaf powder, the 1/n value is ~ 0.72 (<1), which indicates a favorable sorption.

The present data fit the Langmuir, Freundlich and Temkin isotherm models for peepal leaf powder, in the following order: Freundlich(0.995) >Langmuir (0.974) >Temkin (0.913). The monolayer adsorption capacity (Q◦) obtained from Langmuir isotherm model for peepal leaf powder is found to be 2.24 mg/g. The linear relationships as given in table 4 are graphically shown in figure 7, 8 and 9 respectively.

Conclusion

From the above discussions the following conclusions are made: i. The optimum pH for the removal of fluoride by the investigated adsorbents is ~ 7. ii. The optimum adsorbent dose for the investigated adsorbent is 10 g/l for the removal of fluoride from water. iii. The optimum temperature for fluoride removal is ~ 30 ^{0} C. iv. Freundlich isotherm gives well prediction of the equilibrium adsorption (R^2 = 0.995). v. The specific uptake increases from 0.09 mg/g to 1.48 mg/g with the increase in initial fluoride concentration from 1 mg/L to 20 mg/L. vi. Maximum specific uptake obtained from Langmuir isotherm is found to be 2.24 mg/g. vii. When the initial fluoride concentration is 5mg/L, the removal efficiency of peepal leaf powder is 85.7% so that the fluoride concentration at the treated water is below the permissible limit.

Table-3
Process parameters for optimum removal of fluoride from simulated synthetic industrial waste water using peepal leaf powder

Parameters	Optimum Value	Specific uptake (mg/g)	% Removal	Remarks
Agitation time, (min) pH Dose (g/L) Temperature (^{0} C) F_0 (ppm)	45 7 10 30 20	1.48	74.2 for peepal leaf powder	Equilibrium reaches at an agitation period of 45 min.

Table-4
Equilibrium models

Freundlich model	$\log q_e = \log K_f + 1/n \log C_e$	K_f((mg/g)/(mg/L), 1/*n*) and nare the constant
Langmuir model	$C_e/q_e = 1/Q^0 b + C_e/Q^0$	Q^0 is q_{max} (mg/g), and *b* (L/mg) is the Langmuir constants related to the capacity and energy of adsorption.
Temkin model	$q_e = B \ln A + B \ln Ce$	*A* and *B* are the temkin constant

Table-5
Equilibrium parameters

Isotherms	Parameters	Values
Freundlich	R^2	0.995
	N	1.38
	1/n	0.72
	K_f	0.30
Langmuir	R^2	0.975
	Q^0	2.24
	B	0.32
	R_L	0.13
Temkin	R^2	0.913
	b	0.79
	a	0.74

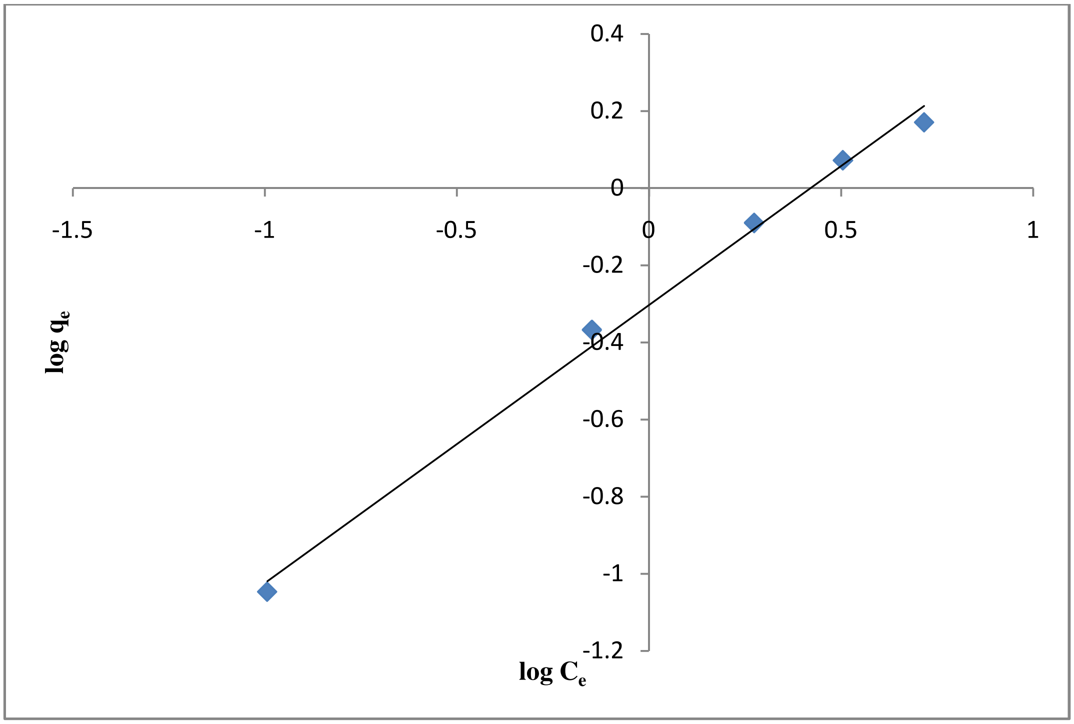

Figure-7
Freundlich isotherm model for adsorption of fluoride on to peepal leaf powder; (Process conditions: temp: 30^{0}C, pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 45 min)

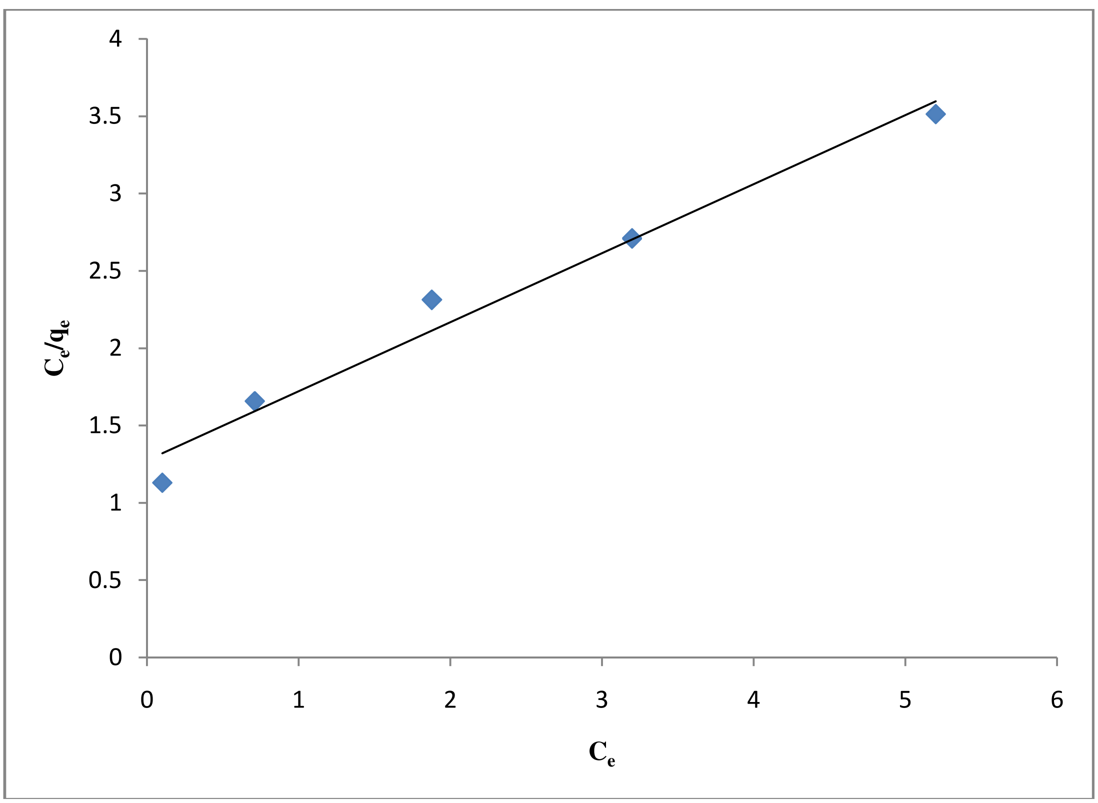

Figure-8
Langmuir Isotherm model for adsorption of fluoride on to peepal leaf powder; (Process conditions: temp: 30^{0}C, pH: 7, concentration of adsorbents: 10g/L, rpm: 125, time: 45min)

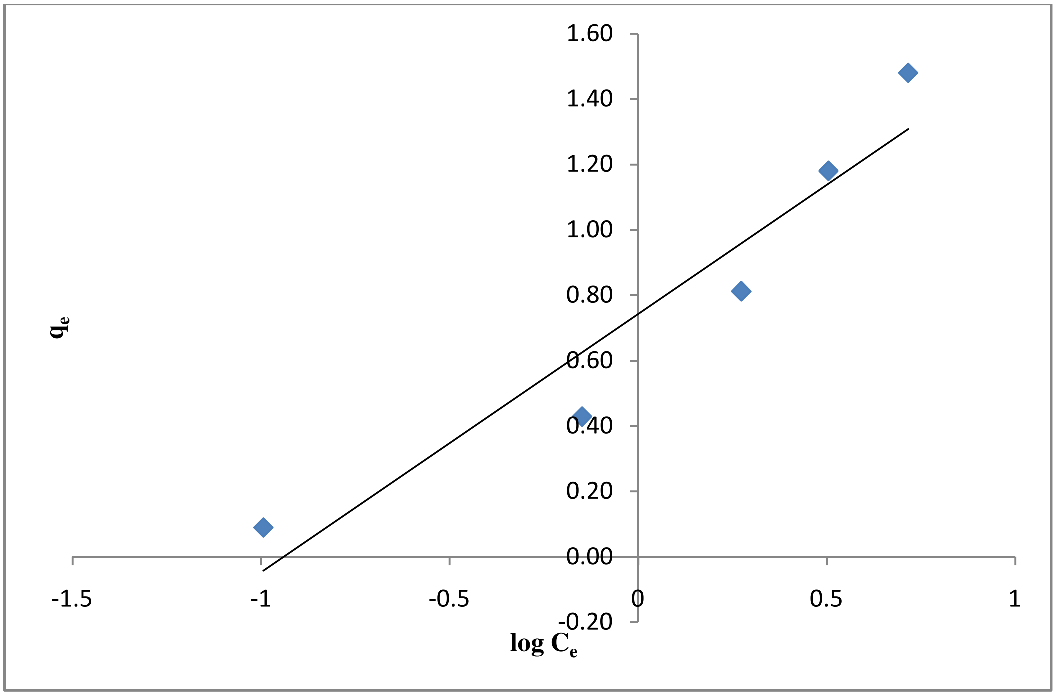

Figure-9
Temkin isotherm for adsorption of fluoride on to peepal leaf powder; (Process conditions: temp: 30 ^{0}C, pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20mg/L, rpm: 125, Time: 45 min)

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