



Removal of Fluoride using *Citrus limetta* in batch Reactor: Kinetics and Equilibrium Studies

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Abstract

The present work deals with the removal of fluoride from synthetic water using mosambi (*Citrus Limetta*) peel powder in a batch reactor. The effects of time and initial concentration of fluoride on the % removal have been studied. Kinetics parameters and equilibrium constants have been computed from various kinetic and equilibrium models. Adsorption of fluoride on to *Citrus Limetta* obeyed the pseudo second order rate equation. The equilibrium data were found to fit well with Freundlich isotherm for adsorbent.

Keywords: Fluoride, bioadsorption, *Citrus Limetta*, water.

Introduction

Releases of chemicals in industrial waste water which produce toxicity include: inorganic chemicals and organic chemicals. Even in very low concentration, these chemicals may be toxic to aquatic life as well as terrestrial life. Therefore, treatment of these toxic materials is required before its discharge. Fluoride is the major inorganic pollutant of natural origin found in groundwater. Fluorine (F) is an element of the halogen family. It forms inorganic and organic compounds called fluorides. When the level of fluoride in water is beyond its permissible limit, it is responsible for various types of fluorosis among human being. 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.

Fluoride enters into groundwater due to dissolution from minerals/ rocks like topaz, fluorite, fluorapatite, cryolite, phosphorite, fluorapatite, etc available at the aquifer bottom³. It enters the soil through weathering of rocks, precipitation or waste run off. Further, a number of industrial processes such as coal combustion, steel production, and other manufacturing processes (aluminium, copper and nickel production, phosphate ore processing, phosphate fertilizer production, glass, brick and ceramic manufacturing) etc. also contribute to increase fluoride levels in water. There are many processes available such as adsorption, ion exchange, electro dialysis, coagulation/precipitation, dialysis, reverse osmosis, nanofiltration, ultrafiltration etc., for the removal of fluoride from water⁴⁻¹⁷. All these processes have their intrinsic advantages and limitations such as less efficiency, sensitive operating conditions, production of secondary sludge in application. However, 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 attention 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 rice husk ash, neem leaf, peepalleaf, khair leaf, tamarind fruit shell etc.¹⁸⁻²⁰. In most of these literature the concentration of fluoride is in between (1.5-5 mg/l), normally available in ground water. However, industrial wastewater normally contains higher fluoride concentration²¹ and there is very few literature on the removal of fluoride from water containing fluoride at higher concentration. Further, mosambi peel has hardly been investigated for fluoride removal from water. Therefore, in this work the potential of *Citrus limetta* (mosambi) fruit peel, an agro- based biomass, has been explored for the removal of fluoride from water. The effects of contact time and initial fluoride concentration on the removal of fluoride have been studied and kinetic and equilibrium parameters have been estimated.

Models: To understand adsorption phenomena two types of models are normally developed. The first type is on the basis of agitation period (kinetics model), and the second type is on the basis of initial fluoride concentration (equilibrium model) as follows.

Kinetic Models: Pseudo first order model: In 1898 Lagergren obtained a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption and it is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity^{22,23}.

$$\log (q_e - q_t) = \log(q_e) - (K_1 / 2.303)t \quad (1)$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively.

The rate constant (K_1) and theoretical equilibrium sorption capacities (q_e), are calculated from the slope and intercept of the linear plots of the pseudo-first-order kinetic model.

Pseudo-second order model: The pseudo second order kinetic model²⁴ is expressed through equation 2.

$$t/q_t = 1/K_2q_e^2 + t/q_e \quad (2)$$

Where k_2 is the pseudo-second-order adsorption rate constant (g/mg s). At $t=0$, $k_2q_e^2$ represents the rate of adsorption, and, hence, it is termed as initial adsorption rate h (mg/g s). Plot of (t/q_t) vs t should give a linear relationship which allows computation of K_2 , and q_e .

Intraparticle diffusion model: Intraparticle diffusion model can be applied to examine the effects of the intraparticle diffusion on the fluoride removal process and boundary layer effects. According to this model the adsorbate moves from the solution phase to the surface of the adsorbent particles, in several steps^{25,26}. The whole adsorption process may be controlled by one or more steps viz pore diffusion, surface diffusion, film or external diffusion, adsorption on the pore surface or a combination of more than one step.

This diffusion model has been broadly applicable in adsorbate-adsorbent systems. The theories of this model were developed by Weber and Morris (1963) as presented through equation 3²⁷.

$$q_t = K_{id}\sqrt{t} + C \quad (3)$$

Where, q_t is sorbed concentration at time t ; K_{id} is rate constant of intraparticle transport (mg/g/time^{1/2}) and C (mg/g) is the intercept that gives an idea about the thickness of the boundary layer. Values of K_{id} and C can be determined from the slope and intercept of the q_t vs $t^{1/2}$ plot.

Elovich model: A kinetic model of chemisorption was developed by Zeldowitsch in 1934. Previously Elovich's equation has been widely used to describe the adsorption of gas onto solid systems. Recently it has also been applied to describe the adsorption process of pollutants from aqueous solutions²².

The Elovich model equation is usually expressed as follows²⁰

$$Dq_t/dt = \alpha \exp(-\beta q_t) \quad (4)$$

$$q_t = \beta \ln(\alpha/\beta) + \beta \ln t \quad (5)$$

Where q_t is the sorption capacity at time t (mg/g), α is the initial sorption rate (mg/g/min) and β is the desorption constant (g/mg). The constants can be obtained from the slope and the intercept of a straight line plot of q_t vs $\ln t$.

Equilibrium model: Freundlich isotherm model: The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface²⁰. Non-linear and linear form of Freundlich adsorption isotherm for monolayer adsorption can be expressed through equation 6 and 7:

$$q_e = K_f \times C_e^{1/n} \quad (6)$$

$$\log q_e = \log K_f + 1/n \log C_e \quad (7)$$

Where K_f and n are the constant that are dependent on various environmental factors.

The plot of $\log q_e$ versus $\log C_e$ should result in a straight line. From the slope and the intercept of the plot, the values of n and K_f can be calculated.

Langmuir isotherm model: According to Langmuir adsorption theory monolayer adsorption takes place on homogeneous sorption sites of equal energy²⁰. The Langmuir adsorption isotherm equation can be expressed through equation 9.

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (8)$$

$$C_e/q_e = 1/Q^0 b + C_e/Q^0 \quad (9)$$

Where, q_e is the amount of solute adsorbed per unit weight of the adsorbent at equilibrium (mg/g).

C_e is the equilibrium concentration of the solute in the bulk solution (mg/L), Q^0 is the maximum monolayer adsorption capacity (mg/g), b is the Langmuir constant related to the adsorption energy (l/mg)

A very important characteristic of Langmuir isotherm is a dimensionless separation factor R_L which is defined by Weber and Chakravorti in 1974²⁵. According to them

$$R_L = \frac{1}{1 + b C_0} \quad (10)$$

Where C_0 and b are the initial fluoride concentration and Langmuir constant respectively. By using the separation factor value, the shape of isotherm can be assessed whether it is linear, favorable or unfavorable as in following way.

$R_L > 1$: unfavorable, $R_L = 1$: linear, $R_L < 0$: irreversible, $0 < R_L < 1$: favorable.

Temkin isotherm model: Temkin Isotherm follows the mechanism of chemisorption of the adsorbate onto the adsorbent. Free energy of adsorption is a function of the surface coverage as the rate of adsorption decreases as the adsorbed surface coverage increase²⁰. It is represented by equation 11.

$$q_e = a + b \log C_e \quad (11)$$

Where, q_e and C_e are the equilibrium adsorption capacity (mg/g) and the equilibrium adsorbate concentration (mg/L) respectively. a and b are the temkin constant.

Material and Method

Raw *Citrus limetta* (mosambi) fruit was collected from a local market of Muzaffarnagar, UP, India. All other chemicals used in the present study were purchased from LobaChemie, Fisher Scientific and were of analytical grade. Stock solution (100 mg/L) of fluoride was prepared by Milli-Q water (BioPAK Polisher, L. No. F2NA57203) by dissolving 221 mg anhydrous sodium fluoride in one L water²⁸.

Procedure: To conduct experiment on fluoride removal each 50 ml of the synthetic water sample containing 20 mg/L fluoride was added in 100 ml vessel containing 10 g/L bio-adsorbent having particle size of 350 μm , which was followed by shaking at 125 rpm^{19,20}. Ranges of operating parameters for various experiments are shown in table 1.

Table-1

Ranges of operating parameters for time and initial fluoride concentration

Objective of experiment	Operating parameters
To study the effect of time on fluoride removal	AD: 10g/L; IFC: 20mg/L; Temp.: 30°C; solution pH: 7; time: 5, 10, 15, 20, 25, 30, 45, 60 min
To study the effect of initial fluoride ion concentration on fluoride removal	AD: 10g/L; Time.: 30 min; solution pH: 7; Temp: 30 °C; IFC: 1, 5, 10, 15, 20mg/L

AD: Adsorbent dose, IFC: Initial fluoride concentration

In each case, after the adsorption, the solution was filtered through Whatman no 42 filter paper²⁹ and the filtrate was analyzed through SPADNS²⁸ photometric method, at 570nm using the UV-vis spectrophotometer (UV-210 A, Shimadzu, Australia) to determine fluoride concentration. The fluoride concentration retained in the adsorbent phase, q_e (mg/g), was calculated according to following formula³⁰,

$$q_e = (C_i - C_f) \times V / W(1)$$

Where q_e is the amount of fluoride adsorbed (mg/g); C_i and C_f are the initial and residual concentration at equilibrium (mg/L), respectively, of fluoride in solution; W is the weight (g) of the adsorbent and V is the volume (L) of solution.

% adsorption (A) of fluoride was calculated as follows

$$\% A = \frac{(C_i - C_f) \times 100}{C_i}$$

Experimental data on the removal of fluoride from the water generated through the variation of time were used to regress kinetic model equations and compute the kinetic parameters, whereas, equilibrium models were regressed with the data generated through the variation of initial fluoride concentration and isotherm constants were computed.

Results and Discussion

Effect of contact time and initial fluoride concentration on the removal of fluoride species by *Citrus limetta* (mosambi) fruit peel powder along with kinetic and equilibrium study is discussed in the subsequent sections.

Effect of contact time on percentage removal of fluoride and adsorption kinetics: The effect of contact time on the removal of fluoride from synthetic water is shown in figure 1. From figure 1 it is evident that with the increase in contact time the % removal of fluoride increases very fast initially however, above 30 min of contact time the adsorption rate virtually remains constant. At the contact time of 30 min the % removal of fluoride is around 67.4 %.

To find out a suitable kinetic model for explaining the adsorption process pseudo first order model, pseudo second order model, intra particle diffusion model and Elovich model are tested. For this purpose the nonlinear models are first linearized as through equation 1, 2, 3, 4 as described in section 2 and are presented through figure 2 to figure 5.

Kinetic parameters for the above model equations are computed from the slope and intercept of the respective Fig. as stated above and are reported in table 2 along with the values of correlation coefficients (R^2). From table 2 it is clear that pseudo-first order model, pseudo-second model, and Elovich model shows R^2 value of 0.851, 0.998 and 0.887 respectively. However, the errors on the equilibrium specific uptake determined from pseudo first order and pseudo second order equations are ~ -28 % and ~ 6 % respectively. Thus it seems that the kinetics of fluoride adsorption is well explained by pseudo-second order model, which also has maximum R^2 value of 0.998.

Table-2

Kinetic models for Mosambi fruit peel powder

Pseudo- first order model			
$[F]_0$	K_1	Q_e	R^2
20	0.120	0.691	0.851
Pseudo- 2 nd order model			
$[F]_0$	K_2	Q_e	R^2
20	0.221	1.44	0.998
Intra particle diffusion model			
$[F]_0$	K_{id}	C	R^2
20	0.088	0.783	0.754
Elovich model			
$[F]_0$	α	β	R^2
20	62.60	0.215	0.887

$[F]_0$: initial fluoride concentration (mg/L)

Effect of initial fluoride concentration and adsorption equilibrium: 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 0.089mg/g to 1.35mg/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 0.9 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.

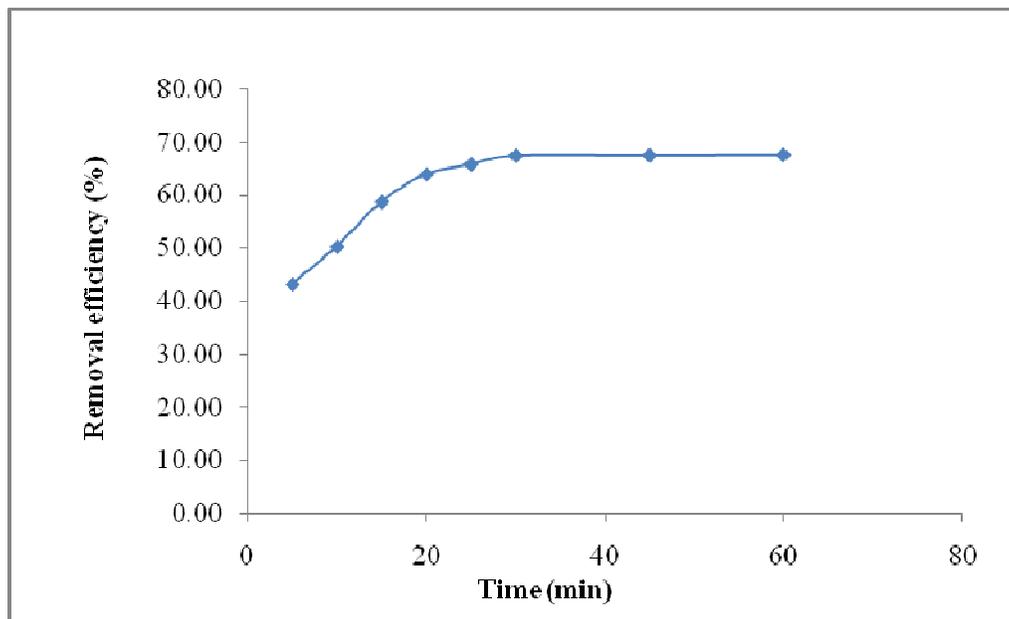


Figure-1

Effect of time on the removal of fluoride species by mosambi peel powder (Process conditions: temp: 30 °C, pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20mg/L, rpm: 125)

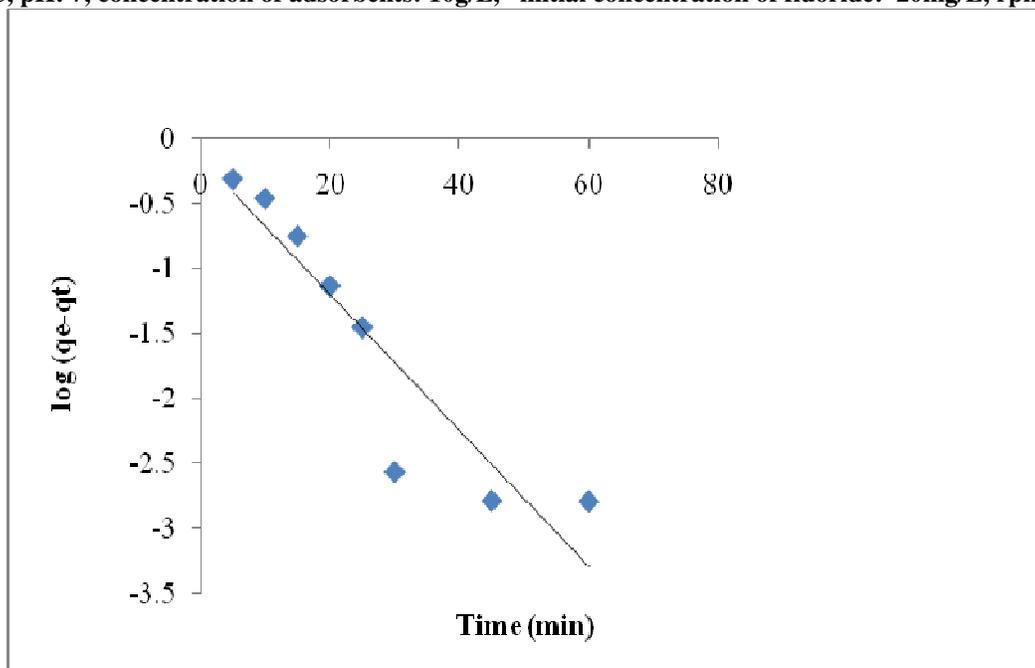


Figure-2

Pseudo first order model for adsorption of fluoride on to *Citrus limetta*; (Process conditions: temp: 30 °C, pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20mg/L, rpm: 125, Time: 30 minutes)

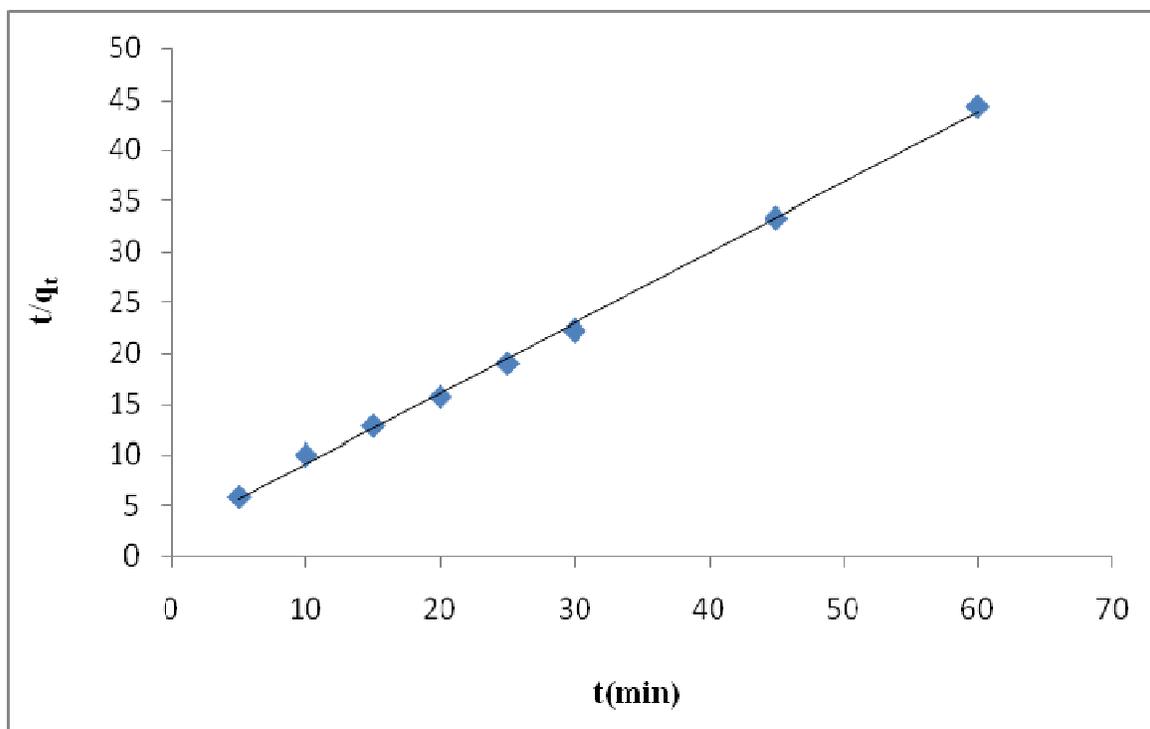


Figure-3

Pseudo second order model for adsorption of fluoride on to *Citrus limetta*; (Process conditions: temp: 30°C, pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20ppm, rpm: 125, Time: 30 min)

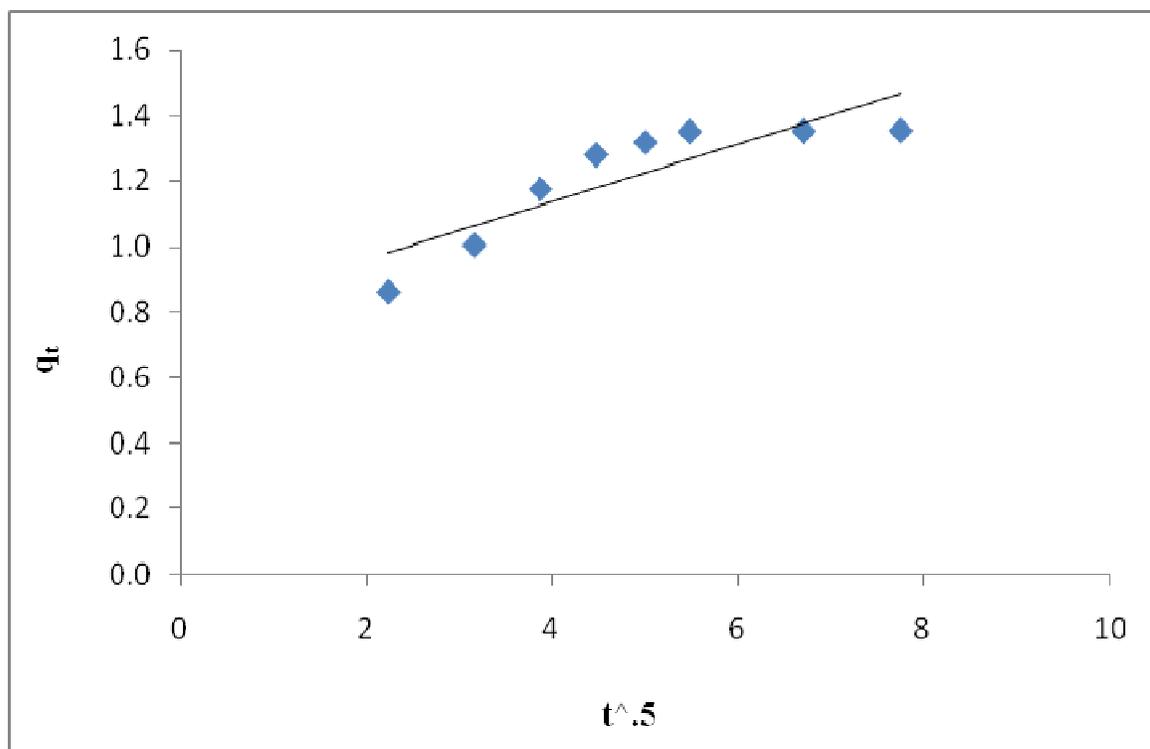


Figure-4

Intra particle diffusion model for adsorption of fluoride on to *Citrus limetta*; (Process conditions: temp: 30 °C, pH: 7, concentration of adsorbents: 10 g/L, initial concentration of fluoride: 20 mg/L, rpm: 125, Time: 30 min)

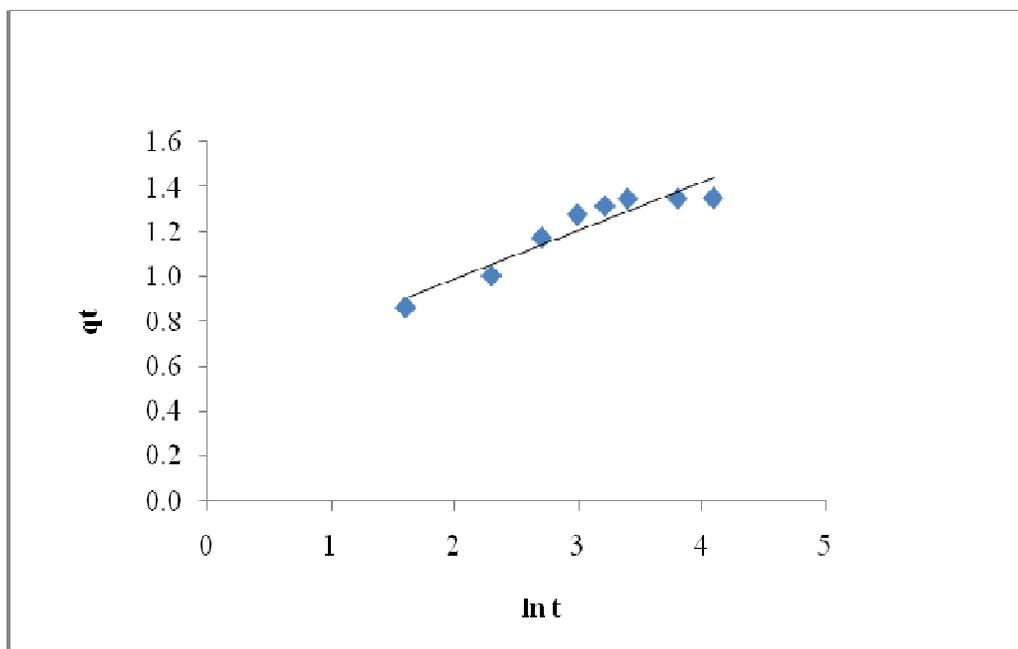


Figure-5

Elovich model for adsorption of fluoride on to *Citrus limetta*; (Process conditions: temp: 30 °C, pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20mg/L, rpm: 125, Time: 30 min)

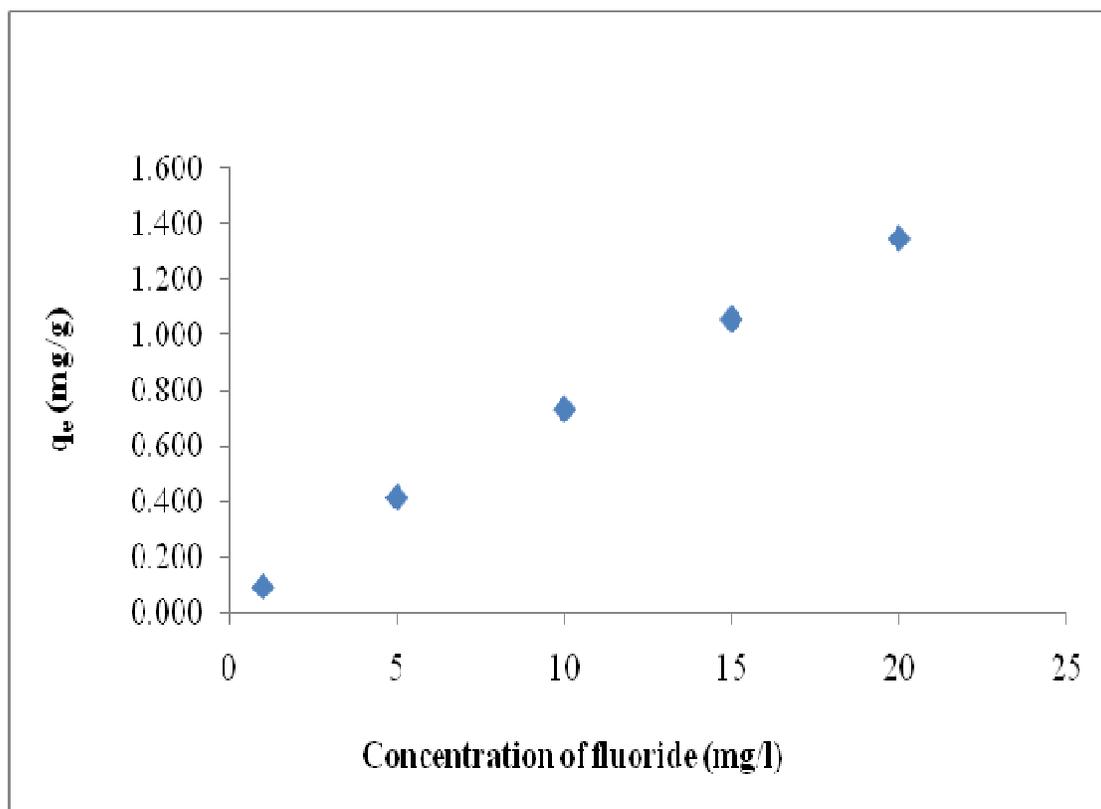


Figure-6

Specific uptake of fluoride by mosambi peel powder (Process conditions: temp: 30 °C, pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 30 min)

To find out a suitable model equation for predicting equilibrium adsorption of fluoride from water Freundlich, Langmuir and Temkin isotherm models have been tested. To find out the isotherm constants the nonlinear models were linearized as per equation 7, 9, 11 as described in section 2. The linear relationships as described through equation 7, 9 and 11 are graphically shown in figure 7, 8 and 9 respectively.

The isotherm constants for the above equilibrium model are shown in table 3 along with R^2 values.

Table-3
Adsorption isotherms

Isotherms	Parameters	Values
Freundlich	R^2	0.996
	n	1.52
	$1/n$	0.657
	K_f	0.40
Langmuir	R^2	0.923
	Q^0	1.82
	b	0.343
	R_L	0.12
Temkin	R^2	0.894
	b	0.663
	a	0.613

In the present work, the R_L values calculated as per equation 10 in the studied range of fluoride concentration are found to be 0.12 which falls in the range of 0–1, which suggests the

favourable sorption of fluoride onto the studied mosambi peel, under the conditions used for the experiments. For mosambi peel, the $1/n$ value is $\sim 0.65 (<1)$, which indicates a favorable sorption.

The present data fit the Langmuir, Freundlich and Temkin isotherm models for mosambi peel, in the following order: Freundlich (0.996) > Langmuir (0.923) > Temkin (0.894). The monolayer adsorption capacity (Q^0) obtained from Langmuir isotherm model for mosambi peel is found to be 1.82 mg/g.

Conclusion

In the present study the fluoride is selected for removal from aqueous solutions using mosambi peel as adsorbent. Batch experiments were conducted to study the impacts of agitation time and initial fluoride ion concentrations. The adsorption kinetics is presented well by pseudo second order rate equation and the estimated equilibrium concentration falls within $\sim 6\%$ error limit. Freundlich isotherm gives well prediction of the equilibrium adsorption ($R^2 = 0.996$). The specific uptake increases from 0.089 mg/g to 1.35 mg/g with the increase in initial fluoride concentration from 1 mg/L to 20 mg/L. Maximum specific uptake obtained from Langmuir isotherm is found to be 1.82 mg/g. When the initial fluoride concentration is 5 mg/L, the removal efficiency of mosambi peel is 82.5% so that the fluoride concentration at the treated water is below the permissible limit.

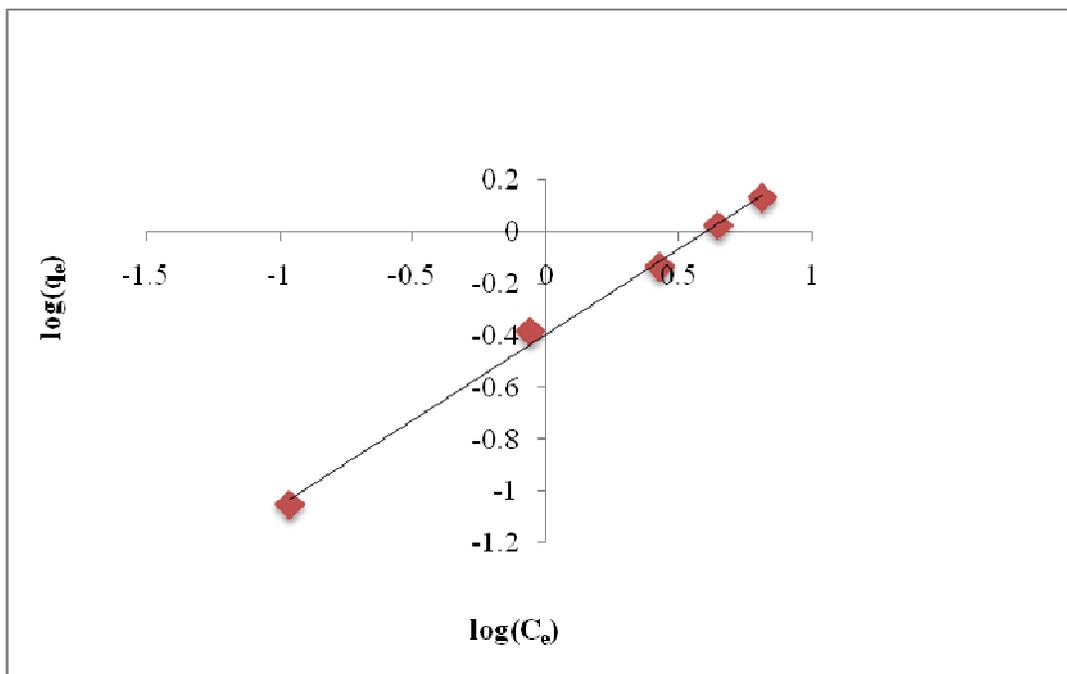


Figure-7

Freundlich isotherm model for adsorption of fluoride on to *Citrus limetta*; (Process conditions: temp: 30 °C, pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 30 min)

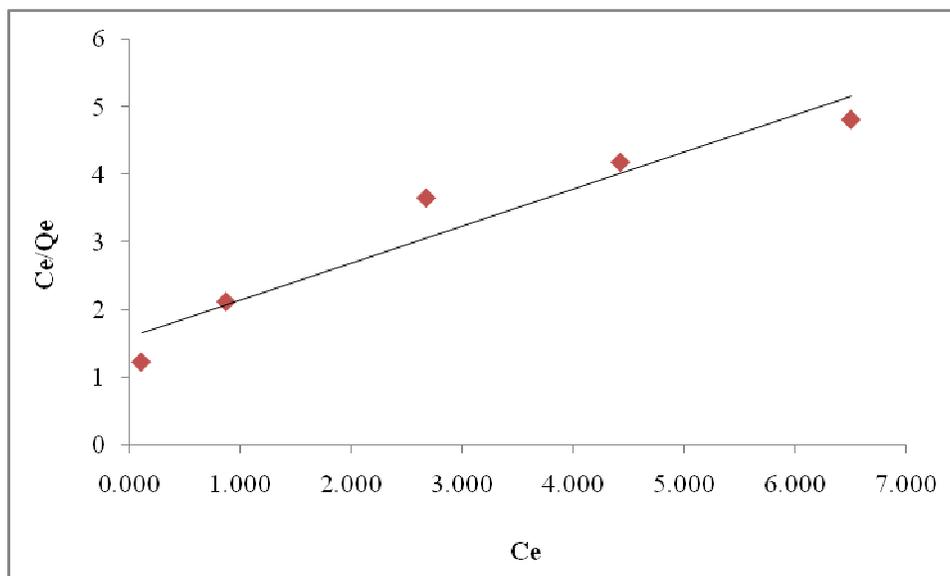


Figure-8

Langmuir Isotherm model for adsorption of fluoride on to *Citrus limetta*; (Process conditions: temp: 30 °C, pH: 7, concentration of adsorbents: 10g/L, rpm: 125, time: 30 min)

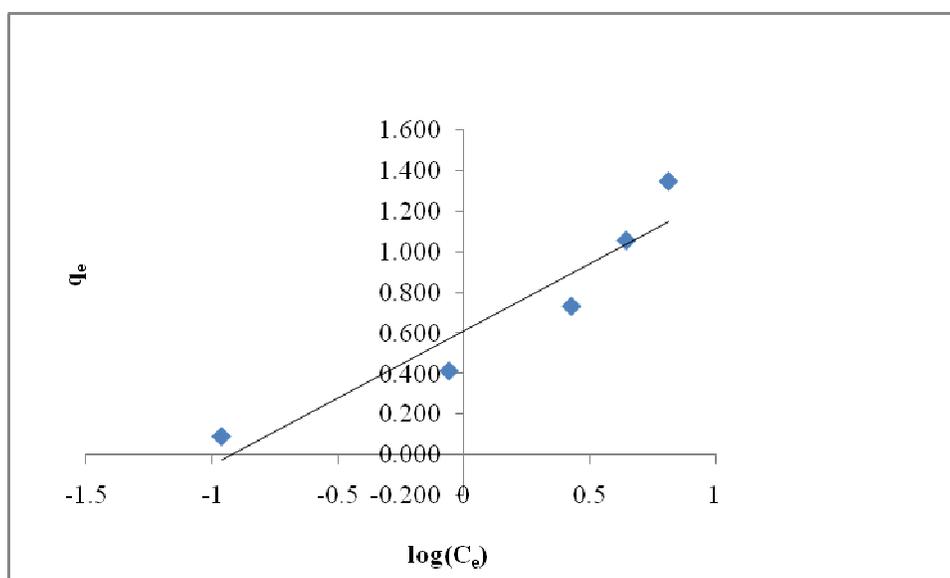


Figure-9

Temkin isotherm for adsorption of fluoride on to *Citrus limetta*; (Process conditions: temp: 30 °C, pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 20mg/L, rpm: 125, Time: 30 min)

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