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Kinetic and Equilibrium Studies of Fluoride Removal Using Ananas comosus peel powder

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ABSTRACT: Water is an important natural resource . It covers around 70% of earth's surface and makes up around 60% of the human body. It is an important resource for both domestic as well as industrial purposes.Water is required for all forms of life and safe drinking water is very important for every living organism.. Pure water is not available at all . Water may be contaminated by natural sources and man made sources.Fluoride is one of contaminant of water. Its permissible limit is 1.5ppm, Beyond this level it is harmful and results in dental fluorosis and skeletal fluorosis. Due to high toxicity of fluoride ions , there is urgent need to treat fluoride contamination. The process of removal of fluoride ions is called defluoridation. This paper deals with removal of fluoride from water by using Ananas comosus(pine-apple)peel powder.

KEY-WORDS: Fluoride,Adsorbent,Langmuir,Freundlich,Kinetic.

INTRODUCTION: Water is a main source of fluoride for living organisms[1]. Fluoride ions enter into water bodies naturally by the process of dissolution of rocks. High amount of fluoride ions enter into the water by excessive use of phosphate fertilizers and pesticides, sewage sludge in agricultural practices [2]. The high levels of fluoride is major cause of dental and skeletal flourosis in rural as well as urban areas [3-5].
Depending on the concentration of fluoride ions in drinking water, the impact of fluoride ions can be beneficial or harmful for human beings[6]. When present within permissible limits(1.5ppm), Fluoride is beneficial for dental enamel because it gives strength to enamel of teeth. And it is required for the maintainance of healthy bones, Beyond this level it is harmful and not suitable [7]. If range of fluoride in drinking water is 1.5–4.0 mg/L then it results in dental fluorosis and higher fluoride concentrations (4–10 mg/L) leads to skeletal fluorosis [8]. .Dental fluorosis is a condition where excess fluoride produce yellow teeth,there are white spots and produce pits in enamel.Skeletal fluorosis is disease of bones. Bones get hardened and become less elastic so there are more chances of fracture.

High fluoride concentrations produce reproduction problems and immunological effects [9].It also interfere in metabolism of carbohydrates, proteins, vitamins and minerals [10].Excess fluoride can results in hyperparathyroidism, which involves uncontrolled secretion of parathyroid hormones. Higher levels of fluoride reduce IQ level[11].

Table : Different Fluoride Concentrations and Their Effects on Human Health

S. No.	Fluoride ion Concentration (mg/L)	Effects on Human Health
1	Below 0.5	Dental caries
2	0.5 to 1.5	Protection against dental caries. Takes care of bone and teeth.
3	1.5 to 3.0	Dental fluorosis
4	3 to 10	Skeletal fluorosis (adverse changes in bone structure)
5	10 or more	Cripping skeletal fluorosis and effects on other organs of body.
6	50	Thyroid malfunctioning
7	125	Kidney malfunctioning

Due to high toxicity of fluoride ions , there is urgent need to treat fluoride contamination. The process of removal of fluoride ions is called defluoridation. There are many techniques of defluoridation like ion exchange technique,membrane filtration technique [12] but those are not in much use because of their high cost and inefficiency.In recent years biosorption has emerged as most suitable technique for the removal of fluoride ions due to convenient operational conditions, low cost, minimum chemical/biological sludge and regeneration properties.

METHODS: Adsorption studies in batch mode were carried out by selected agricultural waste biomass of *Ananas comosus* peel powder (ACPP) for the removal of fluoride ions from water . The effect of pH, initial fluoride ion concentration, bioadsorbent dose and contact time on the removal efficiency was investigated.

The Batch experiment studies were performed by shaking fluoride solution of known concentration with bioadsorbents in shaker. [13,14]. The results were reported in terms of percentage removal and adsorption capacity. The percentage removal (% Removal) of the Fluoride ions was calculated for each run by following expression:

$$\% \text{ Removal} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \qquad 2.1$$

where C_i and C_o were the initial and final concentrations of fluoride ions in the solution.

Further adsorption capacity was calculated in terms of the amount of fluoride ions adsorbed per unit mass of biosorbent by using the expression:

$$Q = \left(\frac{C_o - C_e}{m}\right) \times V \qquad 2.2$$

Where Q (mg/g) is the amount of fluoride adsorbed, C_o (mg/l) is the initial concentration of Fluoride, C_e (mg/l) is the final concentration of fluoride, V is the volume of Fluoride solution(l) and m (g) is the mass of biosorbent used.

Adsorption Isotherms

The sorption isotherms represent the relationship between the amount of fluoride adsorbed by a unit weight of bioadsorbent and the amount of fluoride remaining in the solution at equilibrium.

a)Langmuir Isotherm: Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites and the linearized Langmuir equation is represented as follows:

$$(C_e/q_e) = (1/Q_0b) + (C_e/Q_0) \qquad 2.3$$

Where C_e (mg/l) is the equilibrium concentration, q_e (mg/l) the amount adsorbed at equilibrium time and Q_0 (mg/g) is the maximum quantity of fluoride ion per unit weight of the adsorbent to form a complete monolayer on the surface, whereas b (l/mg) is a constant related to the affinity of binding sites with the fluoride[15].

b)Freundlich Isotherm: The Freundlich expression is an empirical equation used to describe sorption on a heterogeneous system. Freundlich equation is represented as follows:

$$Q = K_f C_e^{1/n} \qquad 2.4$$

Logarithmic form of isotherm is given as:

$$log\frac{x}{m} = \log K_f + \frac{1}{n}\log C_e \qquad 2.5$$

Where K_f (l/g) is Freundlich adsorption coefficient and is related to the adsorption capacity. The exponent n, (dimensionless) is adsorption constant that characterizes the energy distribution of the adsorption sites.

Adsorption Kinetics

Different kinetic models such as the pseudo-first order model [16], Pseudo second order reaction rate model [17] were applied to adsorption data in order to study the mechanism involved in the adsorption process. The expression for Pseudo 1st order kinetics is as follows:

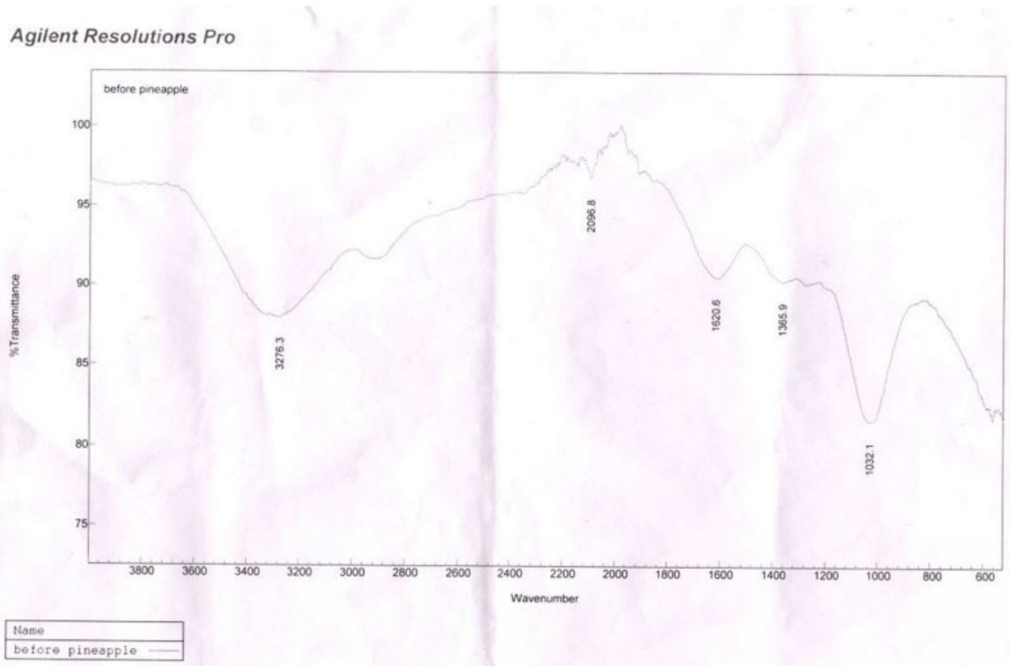
$$\ln (Q_e\text{-}Q_t) = \ln Q_e\text{-}K_1t \qquad 2.6$$

whereQ_e (mg/g) and Q_t (mg/g) are the amount adsorbed of Fluoride ions at equilibrium and at time t, respectively, and K_1 (min^{-1}) is the rate constant of pseudo 1st order adsorption and pseudo second order kinetics is as follows

$$t/q_t = 1/h + 1/q_e\ t \qquad 2.7$$

$h = kq_e^2$ ($mg\ g^{-1}\ min^{-1}$) can be regarded as the initial adsorption rate as $t \rightarrow 0$ and k is the rate constant of pseudo-second order adsorption

RESULTS AND DISCUSSION: Batch experiments were performed by using agricultural waste biomass in natural powdered form of *Ananas comosus* peel powder (ACPP). The effect of various operational parameters was studied by varying the adsorbent dose, contact time, initial fluoride concentration and pH. FTIR studies revealed the participation of various functional groups for the process of deflouridation. FT-IR spectroscopy of ACPP before and after the sorption process indicated the involvement of various functional groups in the adsorption. A prominent shift in the peak of ACPP from 3276.3cm^{-1} to 3312.1cm^{-1} and 1021.1cm^{-1} to 1028.2cm^{-1} suggests the probability of –OH and –OCH_3 groups contributing in the binding of fluoride ions. Slight changes in other peaks before and after fluoride ion sorption imply the probability of surface binding



resulting into fast sorption.

Figure: FTIR studies of native ACPP

Comparison of FTIR frequency data for ACPP native and after loaded with fluoride ions

Frequency (cm^{-1}) Before Adsorption	**Frequency (cm^{-1}) after Adsorption**	**Functional groups present**
3276.3	3312.1	N-H, O-H
2096.8	---	-C≡C- stretch
1620.6	---	C=O stretch, C=C

1385.9	1389.9	C-N
1032.1	1028.2	C-O stretching and bending

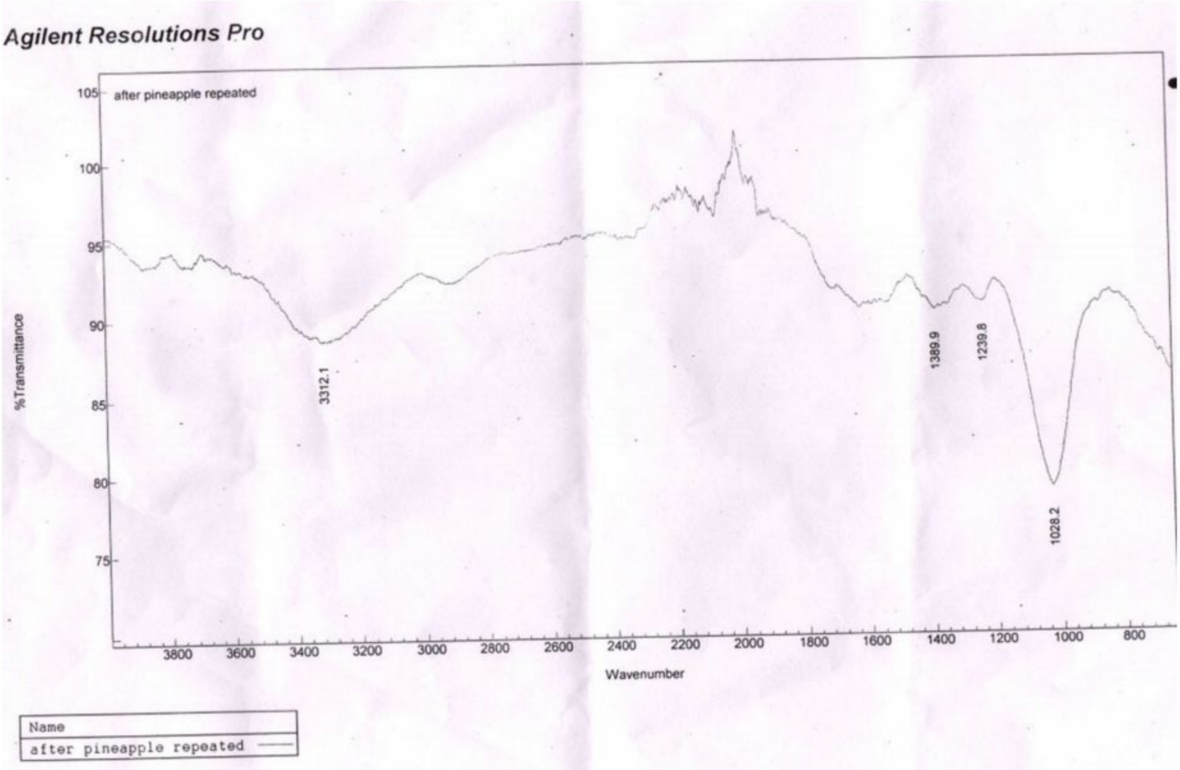


Figure: FTIR of Flouride ion loaded ACPP

Effect of various parameters

1. Effect of pH: A range of pH from 2.0 to 10.0 was selected for the present study keeping all other parameters constant. Maximum adsorption of fluoride was found at pH 4.

Table : Effect of pH on fluoride ion removal

pH	Initial Conc. in mg/l	Final Conc. in mg/l	% F removal
2	5	1.75	65

4	5	0.75	85
6	5	1.25	75
8	5	3.0	40
10	5	2.78	44.5

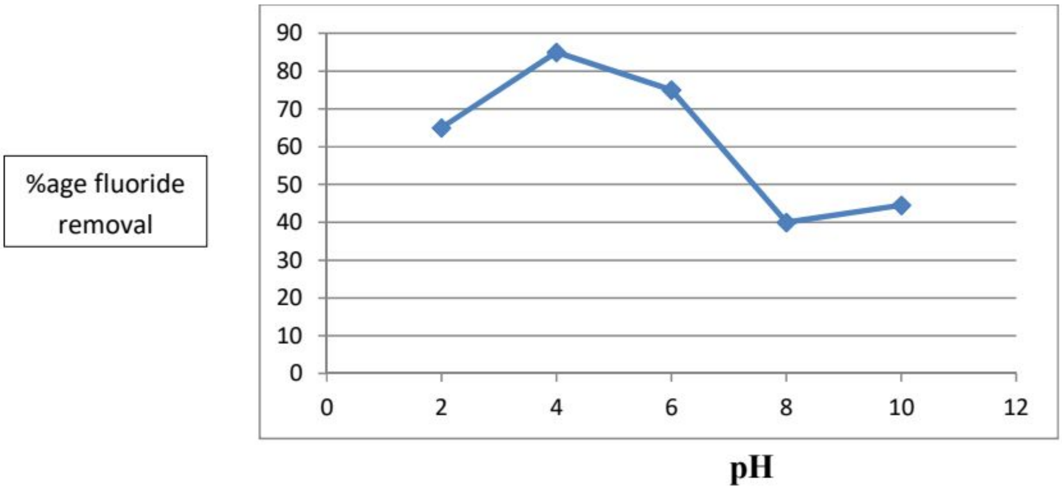


Figure : Effect of pH on the percentage removal of fluoride ions

2. Effect of contact time: As contact time plays a major role in the removal efficiency of fluoride ions so the effect of contact time was investigated by varying the contact time (20-60 min) keeping other parameters constant. The effect of contact time on fluoride biosorption by ACPP is shown in figure.

Table : Effect of contact time on adsorption by ACPP

Contact time in Minutes	Initial Conc. in mg/l	Final Conc. in mg/l	% Flouride Removal
20	5	2.25	55
30	5	2.1	58
40	5	2.0	60
50	5	1.8	64
60	5	1.6	68

Graph between percentage of F^- adsorption and contact time (min) is shown as below. It was found that adsorption quantity of fluoride ion on pineapple peel increases as the contact time increased.

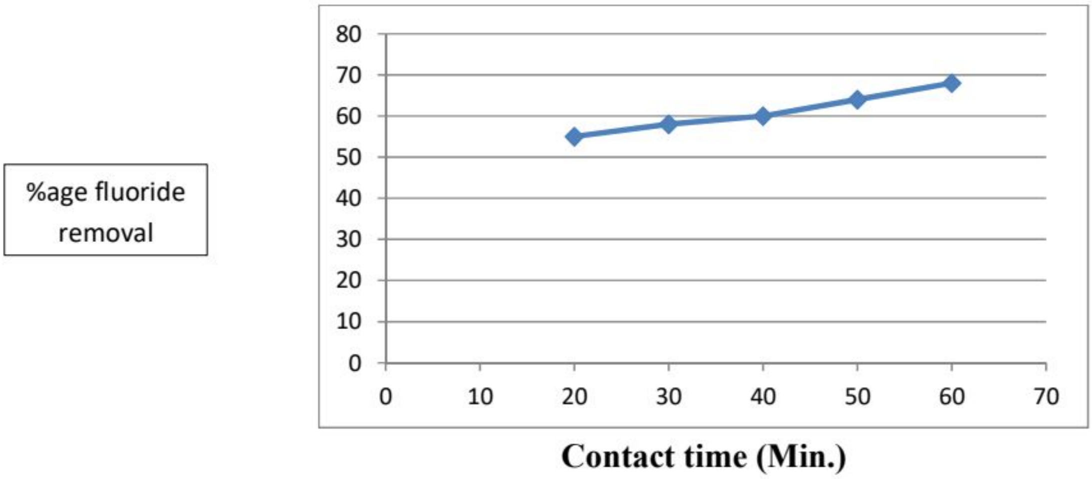
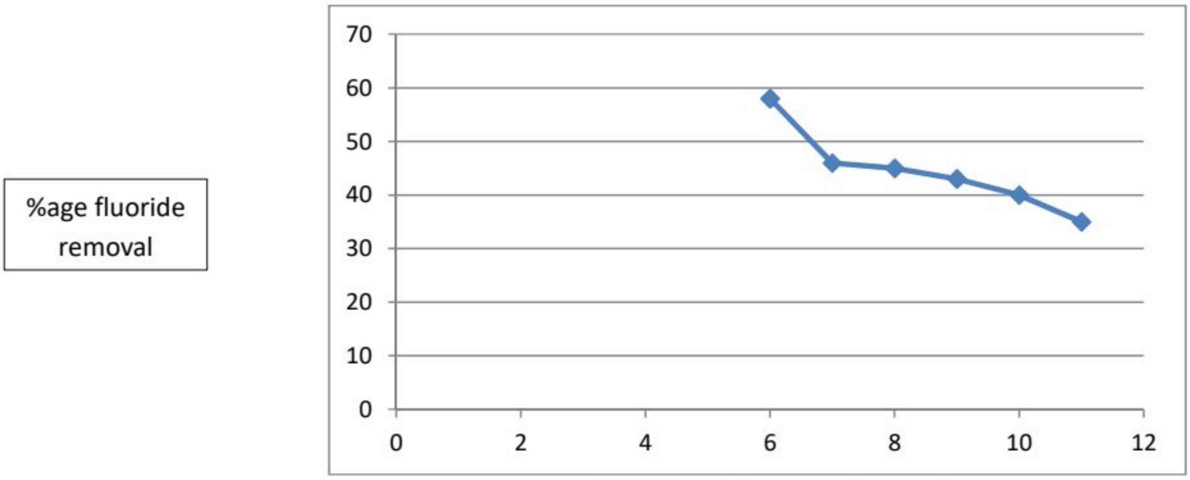


Figure : Effect of contact time on the percentage removal of fluoride ions

3. Effect of initial fluoride ion concentration: Experiments were conducted by varying the initial fluoride ion concentration from 5 ppm to 9 ppm by keeping all other parameters constant. The data shows that with increase in initial fluoride ion concentration, the percentage removal of fluoride ion decreases. So at high conc. adsorption sites are low.

Table : Effect of Initial fluoride ion concentration on adsorption

Initial Conc. in mg/l	Final Conc. in mg/l	% F removal
6	2.5	58
7	3.8	46
8	4.4	45
9	5.1	43
10	6.0	40
11	7.1	35



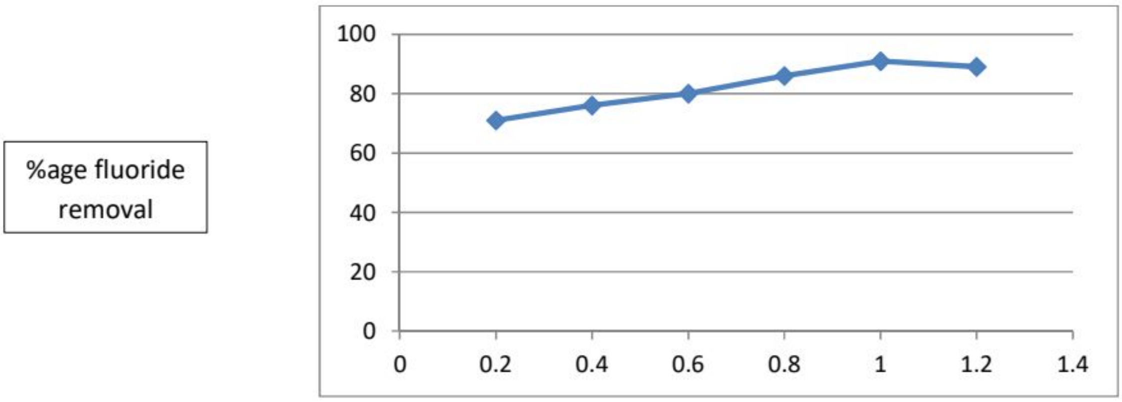
Initial fluoride conc. in mg/l

Figure : Effect of fluoride ion concentration on the percentage removal of fluoride ions

4. Effect of adsorbent dose : The percentage removal of fluoride ion increases with increases in adsorbent doses.

Table : Effect of adsorbent dose on fluoride ion removal

Adsorbent dose in gm	Initial Conc. in mg/l	Final Conc. in mg/l	% F removal
0.2	5	1.45	71
0.4	5	1.2	76
0.6	5	1.0	80
0.8	5	0.7	86
1	5	0.46	90.9
1.2	5	0.55	89



Adsorbent dose in gm

Figure : Effect of adsorbent dose on the percentage removal of fluoride ions

Equilibrium Studies: Two adsorption isotherms i.e. Langmuir, Freundlich isotherms have been applied for the present investigation.

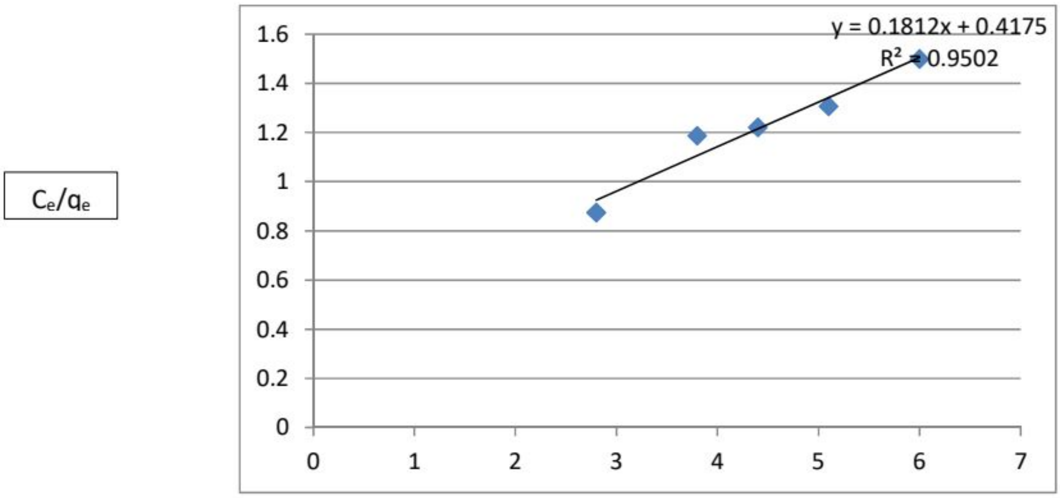
Table 3.23: Various parameters required for Langmuir and Freundlich isotherms

C_i	C_e	X	$x/m=q_e$	C_e / q_e	log C_e	log q_e
6	2.8	3.2	3.2	0.875	0.447	0.5051
7	3.8	3.5	3.5	1.187	0.579	0.5440
8	4.4	3.6	3.6	1.222	0.643	0.556
9	5.1	3.9	3.9	1.3077	0.707	0.591
10	6.0	4.0	4.0	1.500	0.778	0.602

Where C_i = initial conc. of fluoride in solution; C_e = equilibrium conc. of fluoride in solution

m = weight of adsorbent taken; q_e = amount of fluoride adsorbed per unit weight of adsorbent

a) The Langmuir Isotherm: As the model signifies the homogeneous adsorption in which all adsorption sites have equal affinity for the adsorbate so the studies were carried out and data was found good fit with the adsorption isotherm .



C_e

Figure : Langmuir adsorption isotherm for ACPP

From Langmuir isotherm plot

Straight line equation is y = 0.181x + 0.417

$R^2 = 0.950$

$(C_e/q_e) = (1/Q_0b) + (C_e/Q_0)$

$(C_e/Q_o) = mx = 0.181\ x$

$(C_e/Q_o) = 0.181\ C_e$

$Q_0 = 5.49$

$1/Q_0b = 0.4175$

By substituting value of Q_0 we get b=0.436

b) The Freundlich isotherm

Freundlich adsorption isotherm is the relationship between the amount of adsorbate adsorbed per unit mass of adsorbent i.e. q_e and conc. of adsorbate at equilibrium i.e. C_e .

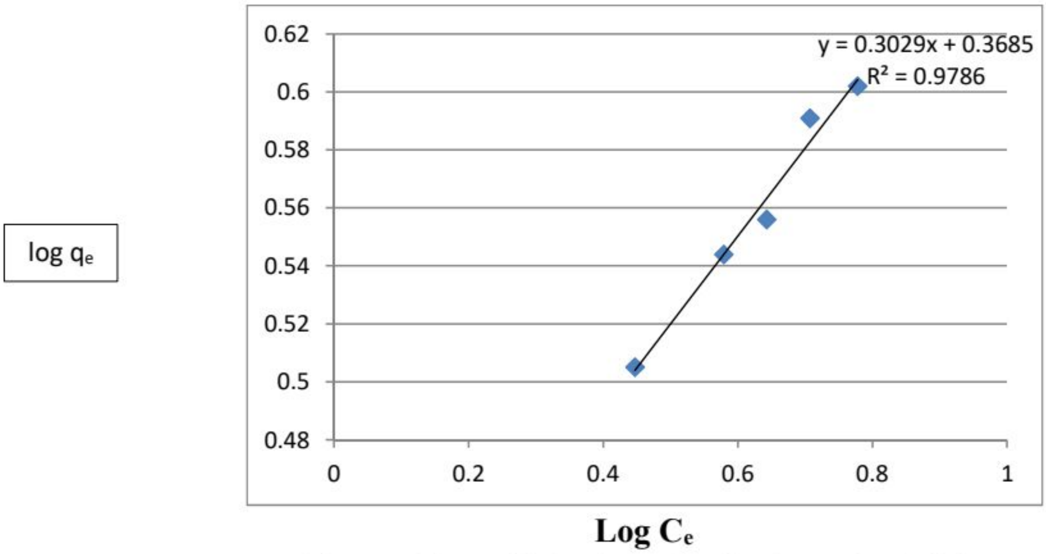


Figure : Freundlich adsorption isotherm for ACPP

From Freundlich isotherm straight line equation is

$y = 0.302x + 0.368$

$1/n = 0.302$

$\log K = 0.368$

$K = 2.33$

$R^2 = 0.978$

The adsorption isotherm for the adsorption of fluoride ions on ACPP is given and the values of adsorption coefficient *(K_d)* and correlation coefficient (R^2) are summarized below in table.

Table: The isotherm model constants and correlation coefficients of ACPP

Langmuir Isotherm	$Q_0 = 5.49$	$b = 0.436$	$R^2 = 0.9502$
Freundlich isotherm	$K = 2.33$	$1/n = 0.3029$	$R^2 = 0.978$

Comparing both isotherms it is clear that ACPP adsorbent fitted Freundlich isotherm better than Langmuir isotherm because of high correlation coefficient.

Kinetic Studies

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first order and pseudo-second order equations were applied to model the kinetics of fluoride adsorption on to ACPP as shown by figures.

Table : Data showing the q_e& q_t values for ACPP

Time in Minutes	C_i	C_e	x	q=x/m	q_e–q_t	log q_e-q_t	t/q_t
20	5	2.25	2.75	2.75	0.65	-0.187	7.27
30	5	2.1	2.9	2.9	0.5	-0.3010	10.34
40	5	2.0	3.0	3.0	0.4	-0.3979	13.33
50	5	1.8	3.2	3.2	0.2	-0.6989	15.62
60	5	1.6	3.4	3.4			

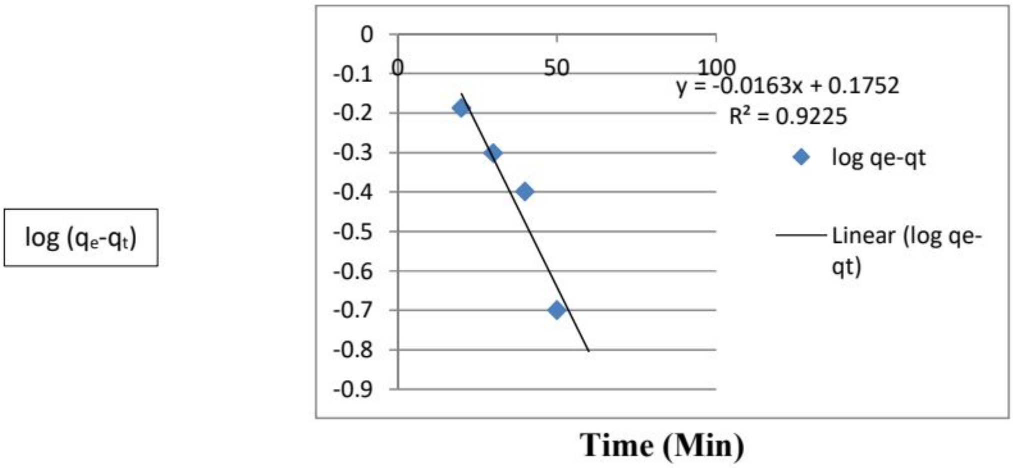


Figure : Pseudo first order reaction for fluoride adsorbed on ACPP

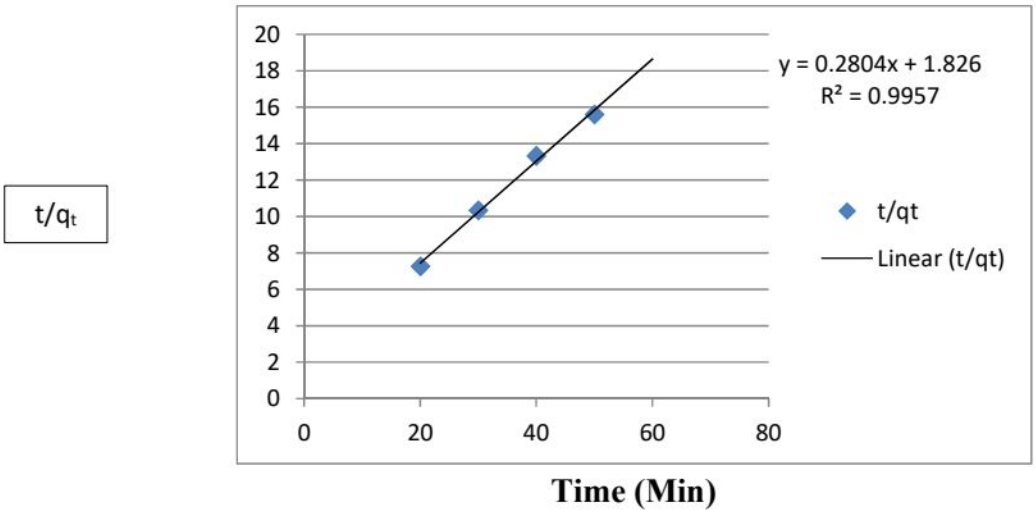


Figure : Pseudo second order reaction for fluoride adsorbed on ACPP

Comparison beween the Adsorption rate constants and correlation coefficient associated with pseudo first order and pseudo-second-order rate equation

a) Pseuo first order rate equation

Kt/2.303=0.0163t

Therefore adsorption rate constant

$K_{ad} = 0.375$

correlation coefficient

$R^2 = 0.9225$

b) Pseudo second order rate equation

$t/q_e = 0.2804t$

$q_{e=}3.566$

$h = kq_e^2$

1/h=1.826

Therefore adsorption rate constant

K = 0.043

correlation coefficient

$R^2 = 0.9957$

Since R^2 obtained from pseudo second order rate equation is greater than R^2 obtained from pseudo first order rate equation, so adsorption by ACPP fits in pseudo second order reaction.

Conclusions: ACPP is good adsorbent for Fluoride.Equilibrium Studies show that it obeys Freundlich isotherm better than Langmuir isotherm because of high correlation coefficient. Kinetic study shows that adsorption by ACPP fits in pseudo second order reaction.

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