Removal Of Noxious Fluoride Ion From Wastewater Using Granular Activated Carbon (Gac): Kinetics And Absorption Studies

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ABSTRACT

Concentration of a Fluoride over a permissible limit is now a worldwide problem and often referred to as 21st century calamity. Almost 372 million people of around 24 countries including Australia, Brazil, Canada, Chile, Ireland, Malaysia, the U.S., and Vietnam are affected by high concentration of Fluoride .The removal of Fluoride from industrial waste water by granular activated carbon(GAC) has been found to be dependent on concentration, pH, contact time, adsorbent dose and temperature .Langmuir and Freundlich isotherm models were used to determine the adsorption parameters. The adsorptive power of fluoride ions on granular activated carbon satisfies not only the Langmuir assumptions but also the Freundlich assumptions i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy. The optimum pH, adsorbent dose, initial concentration and contact time were found to be 4,32g/l, 20mg/l, 120 min respectively.

Keywords: Adsorption; Granular Activated Carbon(GAC) ;Langmuir; Freundlich isotherm models; multilayer formation.

Symbols Used:

q_e = Fluoride adsorbed(mg g^{-1})

C_o = Initial fluoride concentration (mg L^{-1})

C_e = Concentration of fluoride in solution at equilibrium time (mgL^{-1})

V= Volume (L)

m = Mass of adsorbent (g).

A = Fluoride obtained by Curve (mg).

B = Diluted sample final volume (mL).

C =   Diluted sample volume worn for development of color.

A_0 =   Adsorbance at zero fluoride concentration.

A_1 =   Adsorbance at fluoride concentration of 1mg/l.

A_X =   Adsorbance of sample prepared.

q_t =   Adsorption after time t (mg/g)

q_e =   Adsorption at equilibrium (mg/g)

k_1 =   Rate constant for the first order model (h^{-1})

K_2 =   Rate constant for second order model ($g\,mg^{-1}\,h^{-1}$)

C=   The intercept, determined by the thickness of the boundary layer

k_{ip}=   The intra-particle diffusion rate constant.

K_f =   An indicator of the adsorption capacity

n =   Adsorption intensity

R=   Universal gas Constant

T =   Temperature (K)

c_e=   Equilibrium concentration (mg/l)

A_T =   Adsorption constants

b_T=   Adsorption constants

1. INTRODUCTION

The chronic skeletal abnormalities have been observed due to toxicities by excessive waste water skeletal abnormalities. The most common manifestation of the toxicity of fluoride in drinking water is dental fluorosis. Almost 372 million people of around 24 countries including Australia, Brazil, Canada, Chile, Ireland, Malaysia, the U.S., and Vietnam are affected by high concentration of Fluoride(wikipedia).The industries that discharge wastewater containing high fluoride concentrations include glass and ceramic production, semiconductor manufacturing, electroplating, coal fired power stations, beryllium extraction plants, brick and iron works, and aluminium smelters (F.Shen et al. 2003).It is estimated that worldwide about 200 millions of people rely on drinking of water having fluoride concentration more than permissible limit of 1.5mg/l according to guidelines by World Health Organisation (W.H.O 2004).This situation requires a development of simple low cost method for treatment of industrial waste water. In India the water fluoride level varies between 2-29 ppm, as against the maximum allowed limit in drinking water according to Indian Standard (IS 10500, 2005) and guideline of World Health Organization (WHO) is 1.0 - 1.5 ppm. In tropical countries like Mexico, Costa Rica etc. people suffer from skeletal fluorosis, although the concentration of fluoride detected is lower than permissible limit in consumable water. Epidemiological inspection tells us that chronic fluoride toxicity might be influenced by nutritional status. Generally fluoride is dissolved in contaminated water and is easily absorbed by the human body. After which it is distributed all over the body crossing membranes and going into tissues very quickly. In recent decades, human dependency on groundwater increases as we exploit groundwater to meet our need of water. This dependency can be attributed to the scarceness, bacteriological pollution and non-handiness of surface waters in under-developed as well as developing countries.

In order to provide right facilities for safe drinking water for rural areas in India, a large number of tube well, hand pumps etc. are being provided since 1970 because there is hardly any bacteriological contamination in ground water. As a result the number of patients with diseases due to water problem has reduced a lot, but still it leads to appearance of other hazards for health as in major areas of India there is a problem of excess chemical compounds like fluoride and arsenic in groundwater. These issues arise as major among the geo-environmental issues which our country is presently facing (Muhammad F and Anita Ramli 2011).

Many strategies were proposed and examined all over the world for removal of fluoride from water. They are mostly based upon the principles of absorption, ion exchange and precipitation. However, these have several disadvantages limited efficiency, high cost technology, taboo limitations and unnoticeable breakthrough (Nawlakhe et al., 1979). Use of lime, gypsum–fluorite filters, dolomite, granulated bone media, activated carbon, superphosphate, tri-calcium phosphate bone charcoal, magnesite, alum, poly aluminium chloride, activated alumina and aluminium sulphate is needed for carrying out these methods (Phantumvan it et al. 1988). Some methods were used to remove high amount of fluoride from water bodies such as adsorption (Liao and Shi, 2005, Lvl 2007), (Pommerenk and Schafran, 2005), precipitation (Reardon and Wang, 2000), ion-exchange (Castelc et al., 2000), electrodialys is (Amor et al.,2001) and electrochemical methods. Among these, precipitation and adsorption are two most important techniques used for water defluoridation. The concentration of Fluoride in Different Minerals is shown in table 1.1

S.No.	Minerals	Fluoride (mg/L)
1.	Meteorites	28-30
2.	Dunite	12
3.	Basalt	100
4.	High Calcium	520
5.	Granite	- - -
6.	Alkali rocks	1200-8500
7.	Shale	740
8.	Sand stone	270
9.	Deep sea clays	1300
10.	Deep sea carbonates	540

Table 1.1: Concentration of Fluorides in different Minerals(Singh T.P and Majumder C.B 2015)
Some researchers believe that harmful effect caused by fluoride is more than its helpful effects. Table 1.2 provides the effect of amount of Fluoride on our body. (Singh T.P and Majumder C.B 2017)

Concentration of fluoride	Medium	Effects
1 ppm	Water	Dental caries reduction
2 ppm or < 2 ppm	Water	Mottled enamel (dental fluorosis)
8 ppm	Water	10% osteosclerosis
20-80mg/day	Water or food	Crippling skeletal fluorosis

50 ppm	Water or food	Thyroid changes
100 ppm	Water or food	Growth retardation
125 ppm	Water or food	Kidney changes
2.5-5.0g	Acute dose	Death

Table 1.2: Effects of Different Concentration of Fluoride

2. EXPERIMENTAL

2.1 Granular Activated Carbon(GAC)

The adsorbents viz. granular activated carbon is used to adsorb aqueous fluoride from industrial waste water. These were sourced from local old market, Roorkee, India. The GAC was dried, crushed and washed thoroughly with tap water than Millipore water to remove adhering dirt. It was then dried in an oven at 40-60^{0}C for 1 day after which drying material is crushed in jaw crusher and screened in 50μm mesh ASTM.

2.2 The batch adsorption experiment

The stock solution of 100mg/l fluoride was prepared by dissolving 0.221g of anhydrous sodium fluoride (NaF) in one litre of Millipore water. The test solution of 20mg/l fluoride concentration was prepared from stock solution. The selected concentration is the normal fluoride concentration in industrial waste water. All the experiments were carried out in 250 ml conical flasks, with 50 ml test solution at (29+1)C in conical flask in horizontal incubator shaker. At the end of desired contact time, the conical flask was removed from the shaker. Subsequently, samples were filtered using what man no. 42 filter paper and filtrate was analysed for residual fluoride concentration by SPADNS method, described in the standard method of examination of waste water and water (M. Hichour et al. 2000).

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where:

q_e =   Fluoride adsorbed(mg g^{-1})

C_o =   Initial fluoride concentration (mg L^{-1})

C_e =   Concentration of fluoride in solution at equilibrium time (mgL^{-1})

V=   Volume (L)

m =   Mass of adsorbent (g).

The effect of initial fluoride concentration was studied from 20 to 50mg F L^{-1} at a pH 6.9± 0.1. The effect of pH was calculated over the pH range 2 to12 and adjusted using 0.1 M NaOH and HCl solution with an initial fluoride concentration of 20 mg L^{-1} .The effect of contact time (0-60min) was also obtained at different time intervals with an initial fluoride concentration of 20mg F L^{-1} .

2.3 Spectrophoto metric methods

In this technique, a compound of a metal such as aluminium, iron, thorium, zirconium, lanthanum or cerium reacts with an indicator dye to build a complex of small dissociation constant. This complex reacts with fluoride to give a new complex. Because of the transformation in the configuration of the complex, the surface assimilation spectrum also shifts relative to the spectrum for the fluoride-free reagent solutions. This alteration can be observed by using a spectrophotometer. One of the essential dyes employed is trisodium 2- (parasulfophenylazo)-1, 8-dihydroxy-3, and 6- naphthalene disulfonate, generally recognized as SPADNS. Erichrome Cyanine R is one most commonly used dye. The dye reacts with metal ions to give a coloured complex. In the SPADNS method, zirconium reacts with SPADNS to build a red coloured complex. Fluoride discolours the red colour of the complex and therefore the alteration in absorbance can be calculated using a spectrophotometer.

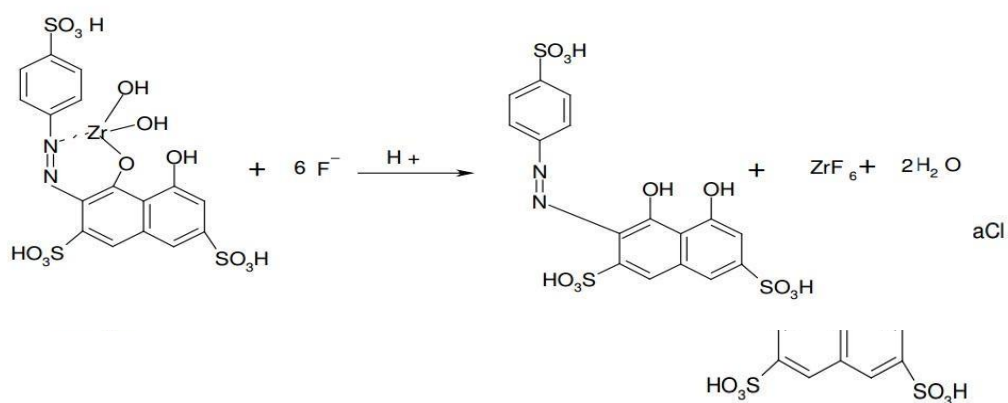### 2.4 Formation of the SPADNS – ZrOCl2 complex

Fig 2.4.1.Reaction of the complex with fluoride ions

2.4.1 Formulation for SPADNS Solution

Where,

$$\frac{Mg\ of\ Fluoride}{Litre} = \frac{A}{Sample\ (mL)} \times \frac{B}{C}$$

A =   Fluoride obtained by Curve (mg).

B =   diluted sample final volume (mL).

C =   diluted sample volume worn for development of color.

$$\frac{Mg\ of\ Fluoride}{Litre} = \frac{A_0 - A_x}{A_0 - A_1}$$

Where,

A_0 =   adsorbance at zero fluoride concentration.

$A_1 =$ adsorbance at fluoride concentration of 1mg/l.

$A_{X} =$ represents adsorbance of sample prepared.

2.5 Adsorption Kinetics

2.5.1 Pseudo First Order Model

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$$

Where,

$q_t =$ Adsorption after time t (mg/g)
$q_e =$ Adsorption at equilibrium (mg/g)
$k_{1 =}$ Rate constant for the first order model (h^{-1})

2.5.2 Pseudo Second Order Model

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2}$$

Where,

$q_t =$ Adsorption after time t (mg/g)
$q_e =$ Adsorption at equilibrium (mg/g)
$K_{2 =}$ Rate constant for second order model ($g\ mg^{-1}\ h^{-1}$)

2.5.3 Intra Particle Diffusion Model

Intra particle diffusion Rate of sorption is frequently used to analyse nature of the 'rate-controlling step' and the use of the intra-particle diffusion model has been greatly explored in this regard which is represented by the following Weber and Morris equation. (Ho Y S et al. 2009)

$q_t = k_{ip} * t^{0.5} + C$

Where,

$q_t =$ Adsorption after time t (mg/g)
C= the intercept, determined by the thickness of the boundary layer
$k_{ip} =$ the intra-particle diffusion rate constant.

According to this model, if adsorption of a solute is controlled by the intra-particle diffusion process, a plot of q_t versus $t^{0.5}$ gives a straight line.

2.6 Adsorption Isotherms

2.6.1 Langmuir Model

Langmuir model is as given in equation (Ghorai and Pant, 2005)

$$q_e = \frac{KaC_e}{1 + aCe}$$

Where K and a are isotherm constants.
Langmuir constant (K) is fluoride adsorbed per unit weight of adsorbent, at equilibrium time. Langmuir constant (a), energy related to adsorption (i.e. affinity of the binding sites). Langmuir equation is valid for monolayer sorption unto a surface with a finite number of identical sites. The

basic assumption of Langmuir model is that sorption takes place at specific sites within the adsorbent. Separation factor is the essential characteristics of Langmuir isotherms can be described in equation below (Bohart and Adams, 1920)

$$R_L = \frac{1}{1 + aC_e}$$

The separation factor (R) indicates the isotherm shape as follows: R < 1 unfavourable, R > 1 unfavourable, R = 1 linear, 0 <R< 1 favourable and R = 0 irreversible.

2.6.2 Freundlich Model

Freundlich isotherm model is given in equation

$$q_e = K_f C^{\frac{1}{n}}$$

Where,

K_f and n are Freundlich constants.

K_f is roughly an indicator of the adsorption capacity and n is the adsorption intensity.

The Freundlich isotherm is used for heterogeneous surface energy systems.

2.6.3 Temkin Model

Temkin Model Equation given as (Hutchins, 1973)

$$q_e = \frac{RT}{b_T}\ln(A_T) + \frac{RT}{b_T}ln(C_e)$$

Where,

R	Universal gas Constant
T	Temperature (K)
q_e	Adsorption capacity (mg/g)
c_e	Equilibrium concentration (mg/l)
A_T	Adsorption constants
b_T	Adsorption constants

3. RESULTS AND DISCUSSIONS

3.1 Effect of pH for Removal of Fluoride by GAC.

The pH of solution significantly affected the adsorbent of fluoride .Adsorption of Fluoride was carried out with various initial pH range 2-11.The more effective removal of fluoride onto the GAC was found at pH of 4-6.Fig 3.1 shows the effect of pH on Fluoride adsorption of GAC .Maximum percentage removal of fluoride was 97.96% found at pH 4. It is observed that removal of fluoride at pH 3 is lower compared to at pH 4-6 as per the speciation of Fluoride, It is present generally as HF instead of anionic fluoride ion (Deng et al. 2011), which could be the reason for less adsorption. At pH 6 and above , the surface of adsorbent came to be deprotonated, which is unfavourable for fluoride adsorption. The Fluoride present as anionic ion however as increasing pH of solution increases, the hydroxide concentration increases which would compute with the fluoride for the adsorptions sites(Thakre et al. 2010).
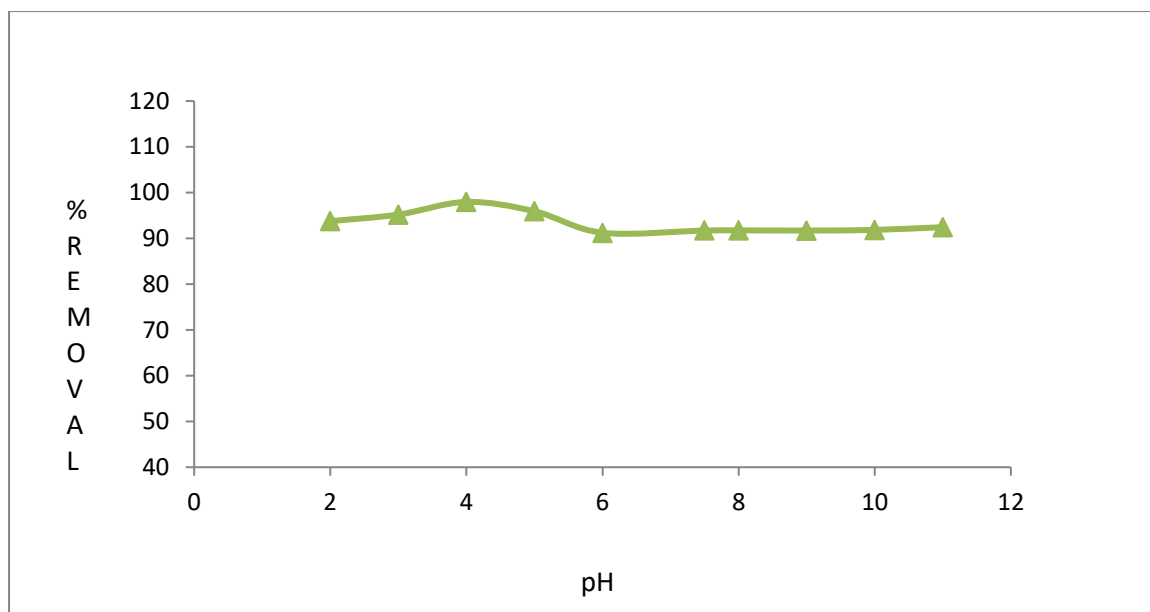
Fig. 3.1 Effect of pH for removal of fluoride by GAC

3.2 Effect of Adsorbent Dose.

Fluoride removal efficiency is dependent on dose concentration of adsorbent.Fig3.2 shows that removal of fluoride enhanced with increasing dose of adsorbent. Higher availability of surface and the pore volume are responsible for enhancing adsorption of solute (Mohammad and Majumder, 2014).As removal was continuously increasing with increase in concentration of dose, after that removal was constant even on increasing concentration. Maximum removal of fluoride was 97.35% at 32g/l dose. It occurred due to the covering of working sites with greater dosage, there by reduction in the net surface area.
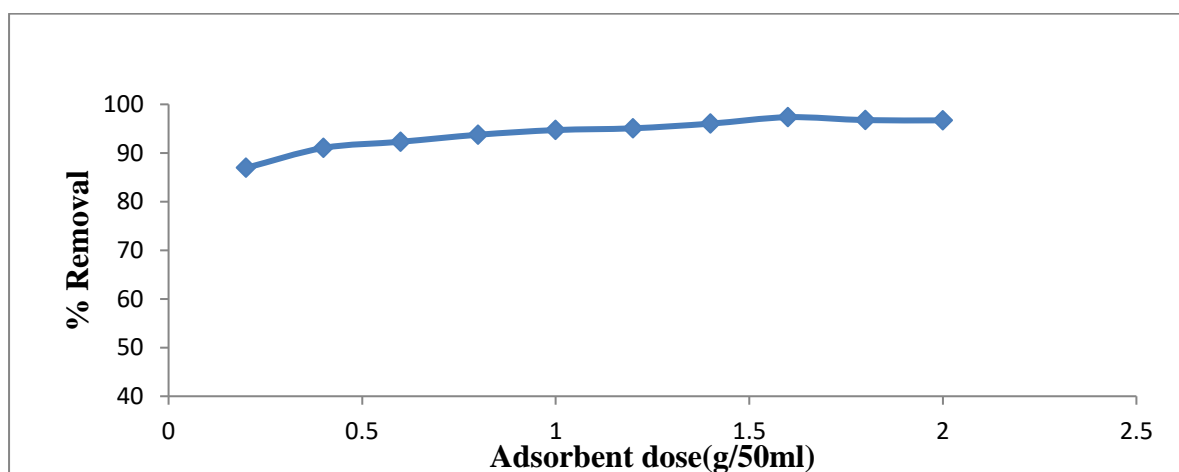
Fig. 3.2 Effect of Dose for removal of fluoride by GAC

3.3 Effect of Contact Time.

From fig 3.2, it was found that the fluoride uptake capacity increase with increase in contact time to some level with optimised pH and dose. Further uptake of fluoride was found constant trend due to

adsorption of fluoride on surface and in to the pore of adsorbent thus less availability of active sites and surface area for further uptake of fluoride and equilibrium stage occurs(Mohan et al. 2004).
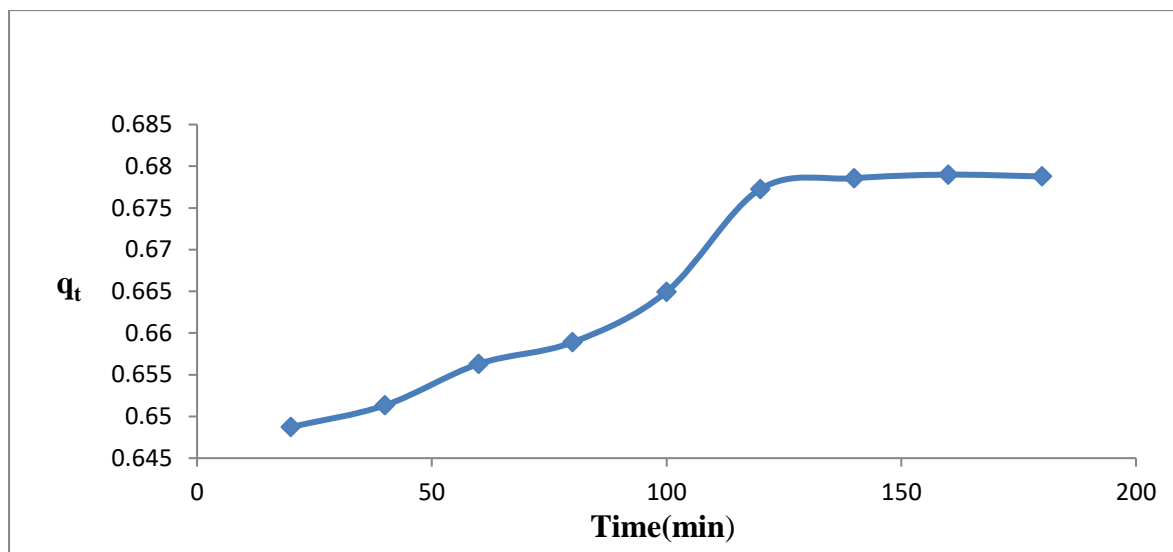

Fig. 3.2 Effect of Contact time for removal of fluoride by GAC

3.3 Effect of Initial Concentration

Initial concentration feed solution of Fluoride on removal percentage is shown in fig 3.3.Initial concentration is varied from 10 mg/l to 30 mg/l.It was indicated in fig 3.3 that the percentage removal of fluoride was decreasing on increasing initial concentration of fluoride due to fixed dose of adsorbent capacity, adsorbent get saturated at high concentration (Mohammad and Majumder,2014; Mohan et al. 2003). Active sites and pore volume occupied with fluoride thus decreased adsorption of Fluoride. Similar kind of trends reported in literature(Chakrabarty and Sarma,2012; Mohan and Karthikeyan,1997).
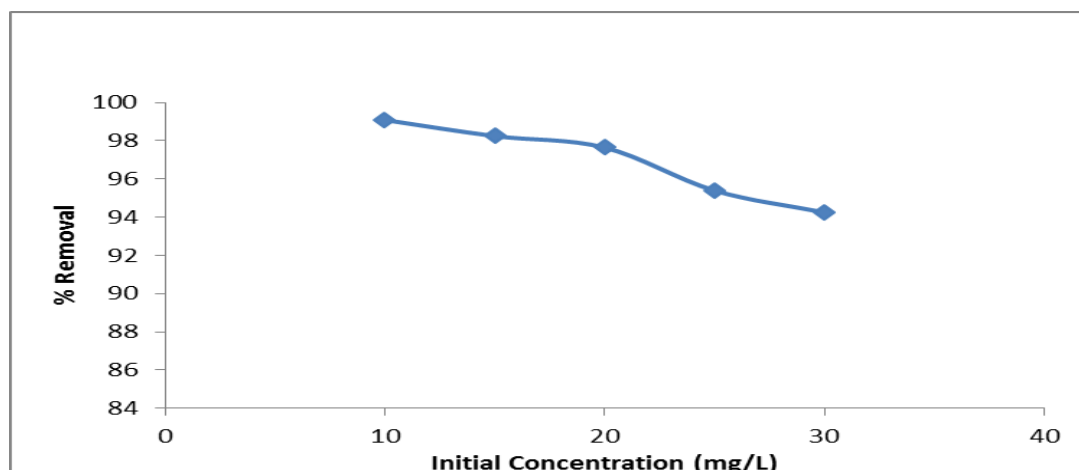

Fig. 3.3 Effect of initial concentration for removal of fluoride by GAC

3.4 Analysis of Granular Activated Carbon (GAC)

3.4.1 FTIR spectrum of GAC before and after adsorption.

Major functional group present in GAC were worked out with the use of Fourier Transform Infrared Spectroscopy(Thermo Nicolet, Magna 7600) both before and after adsorption of fluoride.The samples were prepared by pellet (pressed disk)method by mixing equal amounts of KBr in each sample. The FTIR spectra of GAC before adsorption of fluoride and after adsorption of fluoride in selected range of 4000-400 cm^{-1} are shown in fig 3.4.1(a) and fig 3.4.1(b),respectively which gives evident about the presence of many functional groups on the surface of the GAC.

A broad band between 3100 and 3734 cm^{-1} in FTIR graph is indicative of the presence of both free and hydrogen bonded OH groups on the adsorbent surface. The stretching is due to both the silanol groups(Si-OH) and adsorbed surface. C-O group stretching from aldehydes and ketones can also be inferred from peaks in the region of 1600 cm^{-1}(Wasewar,2009). The peak at 1582 indicated N-H bending and it's shifted to 1575 cm^{-1} due to adsorption of fluoride and the next peak was at 1582 which indicate C=C,C=N stretching of Quinoid ring. Fluoride adsorption was confirmed in range between 1350 and 1100 cm^{-1},which indicate the C-F stretching. Also the wave number 800-400 cm^{-1} indicates the stretching of C-X (X=F,Cl,Br or I) which confirm fluoride adsorption. Wave number shifted from 1393 cm^{-1} to 1398 cm^{-1} assigned the reactivity of carboxylate anion c=o stretching for the adsorption process. A large number of peaks corresponding to various groups disappear after the fluoride adsorption, which indicates utilization of these groups during the adsorption process (Wasewa et al.2009).
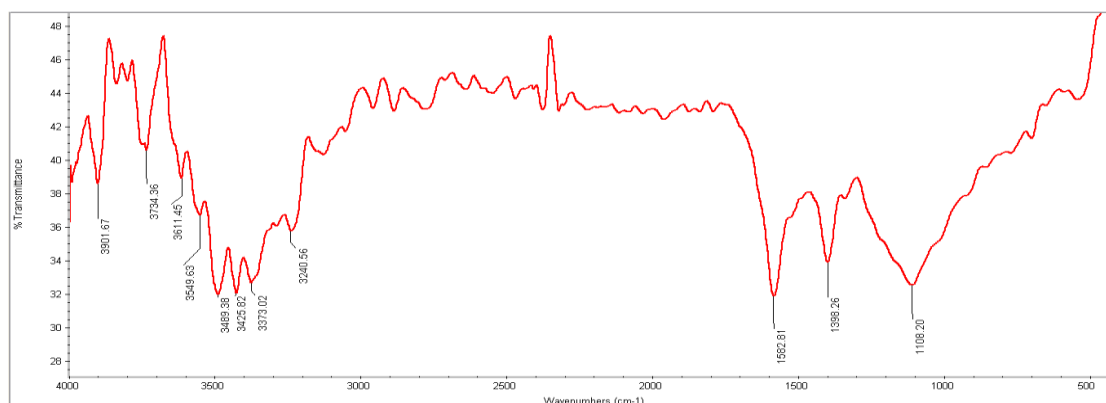

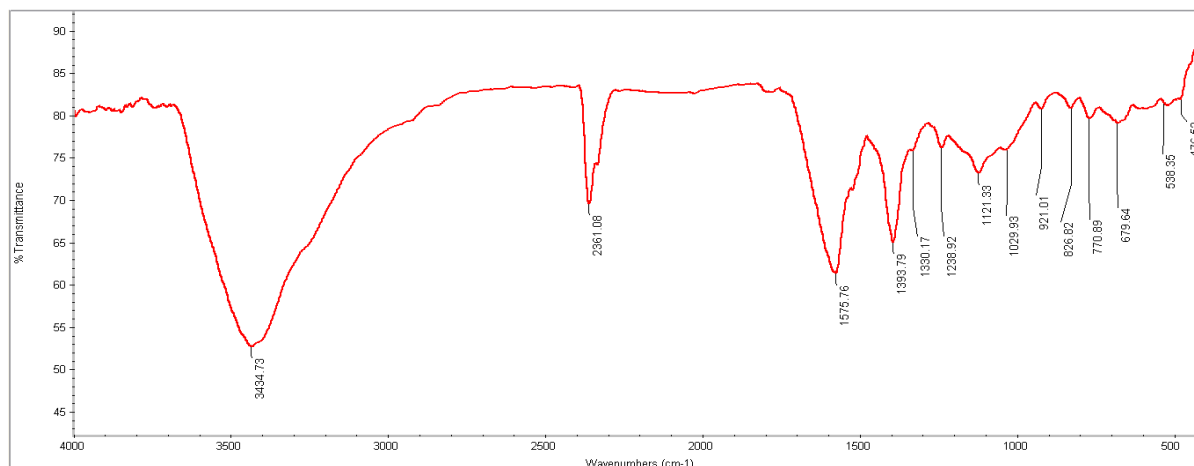**Fig. 3.4.1 (a) FTIR spectra of GAC before adsorption of Fluoride**

Fig. 3.4.1 (b) FTIR spectra of GAC after adsorption of Fluoride

Wave Number(cm⁻¹) Before Adsorption	Wave Number(cm⁻¹) After Adsorption	Groups
3100	3734	Free and Hydrogen bonded OH group.
3434	3434	Stretching due to silanol(Si-OH) group and adsorbed water
1600	-	CO group stretching due to both aldehydes and ketones
1582	1575	N-H bonding
1582	-	C=C,C=N Stretching of Quinoid ring
1350	1100	C-F stretching
800	400	Stretching of C-X (X=F,Cl,Br, or I)
1393	1398	Carboxylate anion C=O stretching

3.4.2 SEM analysis of GAC.

The morphological study of GAC was carried out with Scanning Electron Microscope(SEM).First the sample of GAC was coated with gold in the presence of argon, an inert gas then sample was analyzed with SEM. The fig 3.4.2(a) indicated that SEM images of GAC after adsorption of fluoride .Fig 3.4.2(b) clearly shows that at a 1000X magnifications GAC has highly porous structured and both small and large pore are present. After adsorption of fluoride on the surface GAC and fluoride ions are deposited in inside the pores of GAC and morphological structure of GAC was drastically changed (Wasewar et al. 2009) .
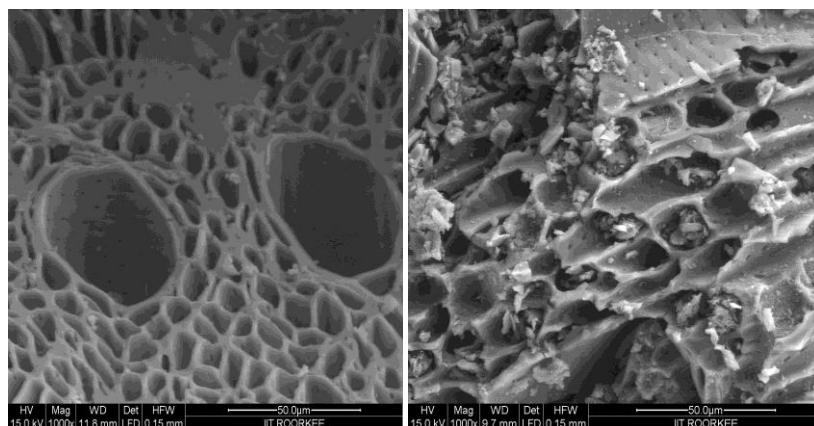
Fig.3.4.2 (a) SEM before adsorptionFig.3.4.2 (b) SEM after fluoride adsorption

3.4.3 EDX analysis of GAC

The EDX analysis of GAC before and after adsorption of fluoride is shown in fig3.4.3 (a) and fig 3.4.3(b) respectively. It is evident that various elements composition of GAC sample before and after adsorption of fluoride are shown in table 3.4.3.1 When the EDX analysis was carried out after the fluoride adsorption, it was found that 0.6% by wt. of the fluoride was present which confirmed the adsorption of fluoride.
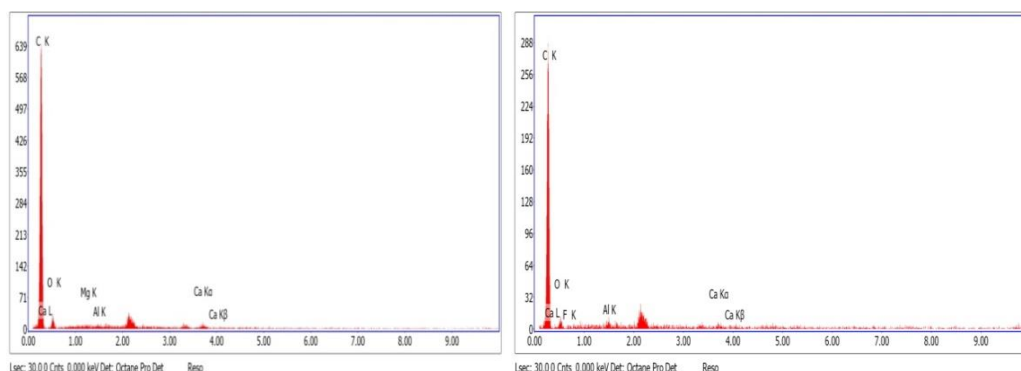

Fig.3.4.3.(a) EDX before adsorption   Fig.3.4.3. (b) EDX after fluoride adsorption

Element	Weight % before Biosorption	Weight % after Biosorption
CK	85.26	86.96
OK	11.96	9.54
FK	--	0.6
AlK	0.3	0.77
CaK	2.08	2.14

Table 3.4.3EDX analysis of GAC before and after adsorption of fluoride in tabular form.

3.5 Adsorption Kinetics for Removal of Fluoride using GAC

The kinetic parameters for the adsorption of fluoride from a synthetic simulated waste on to the surface of GAC have been determined. Many kinetic models like intra particle diffusion, pseudo first order, and pseudo second order are studied in the present study. Studies of these models explain the behaviour of fluoride removal on GAC adsorbents.
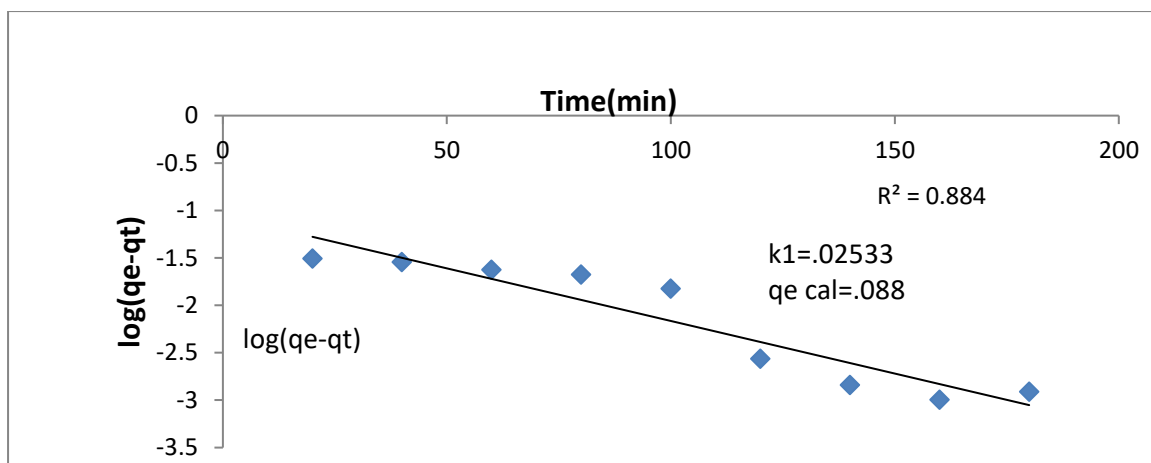
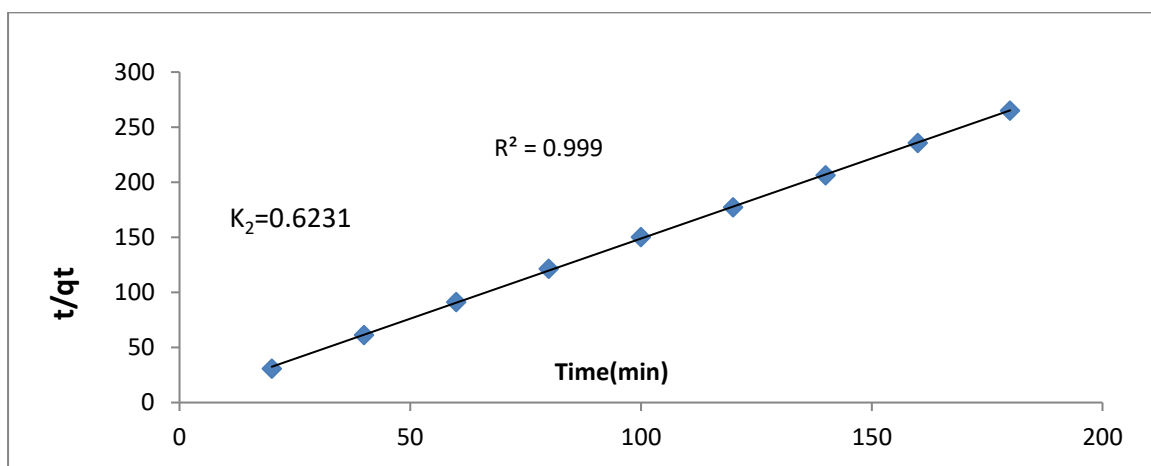**Fig 3.5.1(a) Pseudo First Order Model for Removal of Fluoride using GAC**

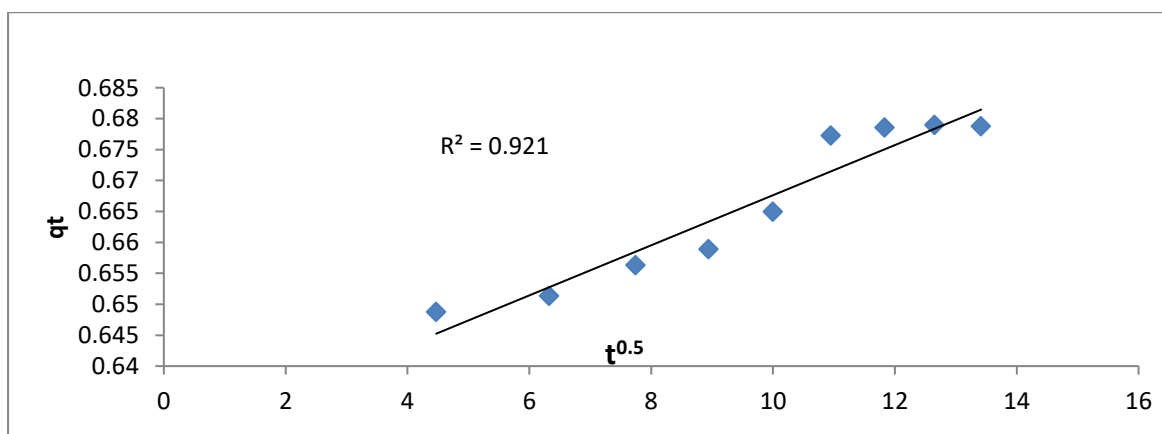**Fig 3.5.1(b) Pseudo Second Order Model for Removal of Fluoride using GAC**

Fig 3.5.1(c) Intra Particle Diffusion Model for Removal of Fluoride Using GAC

Adsorbent	Kinetic Models								
	Pseudo First Order			Pseudo Second Order			Intra-Particle Diffusion		
	K_1	$q_{e(cal)}$	R^2	K_2	$q_{e(cal)}$	R^2	K_P	X_i	R^2
GAC	0.0253	0.088	0.88	0.62	0.688	0.99	0.004	0.627	0.92

Table 3.5.1 Variouskinetic parameters for studied models for GAC.

From table 3.5.1 and fig 3.5.1(a-c), we observed that pseudo second order kinetic fits best from all kinetic models studied for GAC on the basis of maximum correlation coefficient. This gives us the information on possible mechanism of removal of fluoride due to chemisorptions (Lu and Gibb 2008).The equilibrium uptake of fluoride ($q_{e(cal)}$)(.6877 mg/g obtained from pseudo second order kinetics shoes maximum which explains best to the model fits with experimental data.

3.6 Isotherms Study of Fluoride Removal by GAC.

An isotherm study describes the way by which adsorbate interact with adsorbent to attain equilibrium during adsorption process. In present study we used three equilibrium isotherm models (Langmuir, Freundlich and Temkin isotherm models) to understand the equilibrium isotherm for the present system. The Fluoride adsorption isotherm of the GAC adsorbent at optimal pH 4.0 was investigated and the obtained results are shown in Fig 3.6.1(a-c). The experimental data were analyzed by Langmuir, Freundlich and Temkin model equations and the constants are sum marised in table 3.6.1. According to correlation coefficient (R^2), the Langmuir equation is more suitable to describe the adsorption behaviour than Freundlich model and Temkin model which indicate that the uptake may be due to a monolayer adsorption.(Yu et al. 2015)
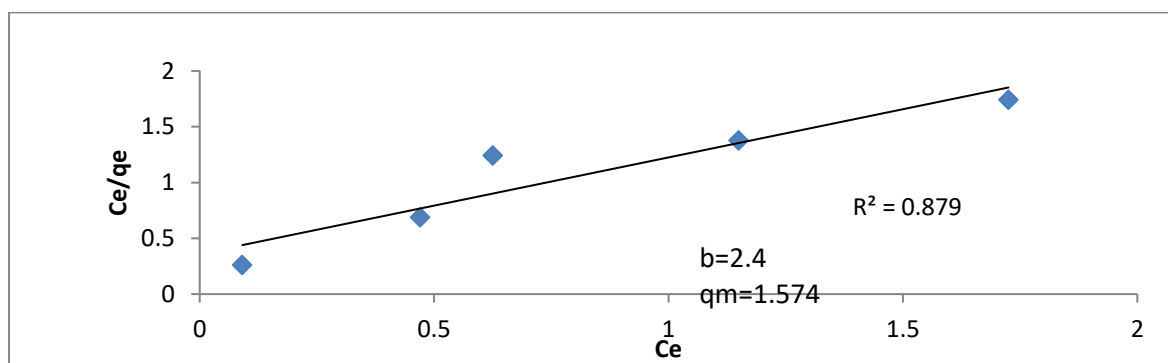

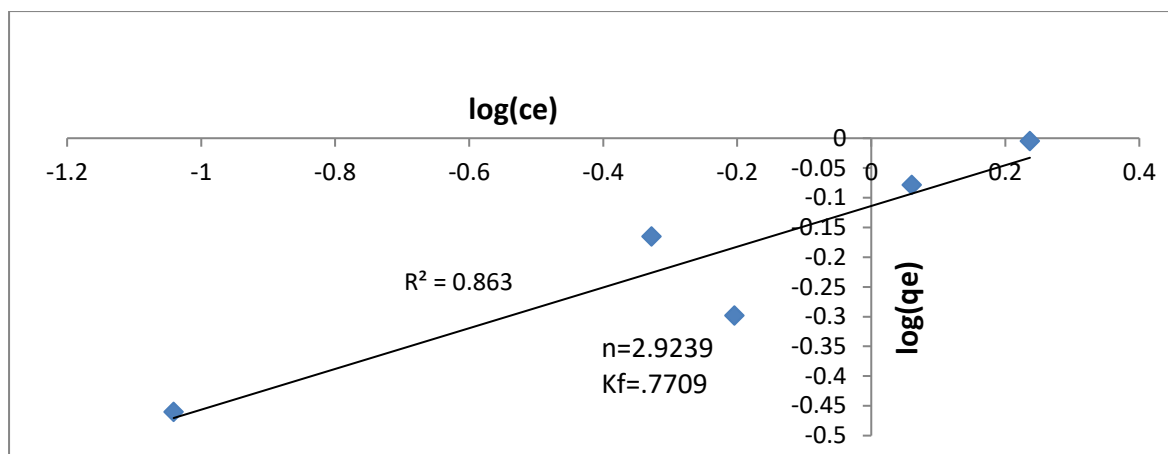**Fig 3.6.1(a) Langmuir Isotherm Model for GAC**
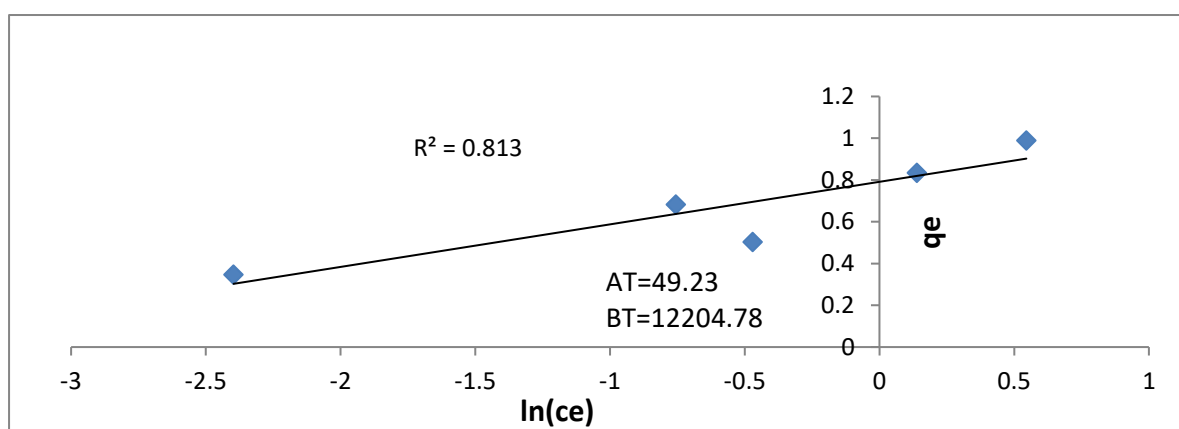
Fig 3.6.1(b) Freundlich Isotherm Model for GAC

Fig 3.6.1(c) Temkin Isotherm Model for GAC

ADSORBENT	Langmuir			Freundlich			Temkin			
	b	q_m	R^2	K_F	n	R^2	A_T	B_T	B	R^2
GAC	2.4	1.57	0.88	0.77	2.92	0.86	49.2	12.2	0.20	0.813

Table3.6.1 Various Isotherm Parameters for studied model for GAC

4.0CONCLUSION

The effect of different parameter on the removal of fluoride by adsorption was carried out up to some extent fluoride removal was increased with increased dose of adsorbent after that removal was found constant on increasing concentration of dose. In contact time effect study it was found that the fluoride uptake capacity increases with increase in contact time up to it equilibrium .The more effective of Fluoride onto the adsorption was found at optimum pH .Removal percentage of fluoride was decreases on increasing initial concentration due to fixed dose of adsorbent capacity adsorbent get saturated at high concentration .

Pseudo second order kinetics fits best from all kinetics model studied for GAC on the basis of maximum correlation coefficient .This gives us the information on the possible mechanism of removal of fluoride due to chemisorptions. It is observed that among three equilibrium isotherm model (Langmuir, Freundlich and Temkin isotherm model) the Langmuir equation is more suitable to describe the adsorption behaviour than Freundlich model and Temkin model which indicate that uptake maybe due to monolayer adsorption.

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