Mechanism of Fluoride Mobilization in an Alluvial Aquifer: a Kinetic Approach

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Abstract: The present research work is executed in order to evaluate the sorption potential of F^- contaminated alluvial aquifer sediments of Birbhum district, West Bengal. The sediment samples are collected from one of the endemic areas of Birbhum district, West Bengal, at a drilled depth of 28 - 32m. Mineralogical studies reveal the presence of quartz, Na-feldspar, K-feldspar and zeolite. Bulk sediment analysis (wt%) indicates the dominance of SiO_2 and Al_2O_3 followed by MgO, CaO, Fe_2O_3, K_2O, Na_2O, TiO_2 and P_2O_5. Batch studies are performed to determine the effects different variables *viz.* pH, sediment dose, interaction time, initial concentration and temperature on sorption-desorption potential of sediment samples. The adsorption isotherm is studied at different temperatures and isotherm profiles offer an excellent fit with Freundlich isotherm with a high R^2 value of 0.977. With respect to different kinetic models the studied sediment samples are more compatible to pseudo second-order kinetics (R^2 0.992). Free energy ($\Delta G°$) suggests an exothermic nature of adsorption. Thermodynamic study reveals that the aquifer sediments have moderate adsorption potential of F^- but have higher desorption potential at neutral to alkaline pH level.

Keywords: Fluoride; aquifer sediment; batch study; Kinetic study.

Introduction

Fluoride contamination of groundwater is a serious problem in several countries spread throughout the world as ingestion of excess F^-, most commonly, through drinking contaminated groundwater causes fluorosis. Mainly two factors are responsible for contamination of groundwater with F^- one is geologic and another is anthropogenic[1,2]. Long term ingestion of F^- in high doses can lead to severe skeletal fluorosis. In India the groundwater of most of the states contains high concentration of $F^{-3,4,5,6,7}$. However, maintaining F^- concentration below the permissible limit (*i.e.,* 1.5 mg/L) in the dietary intake surely minimizes the skeletal and dental problems[8]. Moreover, when the concentration of F^- is above this limit, it causes dental and skeletal fluorosis and lesions of the endocrine glands, thyroid and liver, *etc*. All these serious health effects are observed in different areas all over the world, such as China, India, Mexico, Africa and in some areas of Thar Desert of Pakistan[9]. The prevention of F^- contamination of water is critical; however, F^- removal from water is under practice for several decades to prevent fluorosis.

According to Mondal et al.[16] ion – exchange mechanism is the dominant factor for the mobilisation of F^- in this quaternary alluvial aquifer. Dutta et al.[17] reported that weathering of sediment samples containing muscovite/biotite is the principal mechanism of mobilizing F^- in comparison to the ion – exchange mechanism in silty – clay samples. Hallet et al.[18] studied that a greater potential for F^- mobilization to groundwater from the regolith than the bedrock. But no work has been done on the evaluation of sorption – desorption potential of

F⁻ contaminated aquifer sediment based on kinetic study. With this backdrop the present research work is carried out to find the effect of different variables *viz.* pH, sediment dose, initial concentration of F⁻ ion, temperature and interaction time in mobilizing F⁻ into the aqueous solution.

Materials and methods

1. Collection and processing of bulk sediment sample:

Bore hole sediment sample was collected from a F⁻ contaminated quaternary aquifer of Junitpur, Birbhum at a depth of 28 – 36 m. On the basis of grain size analysis the sample is silty clay/clay in nature. Sample was dried in hot air oven (110°C) and thereafter crushed into a smaller size fraction and sieve passed through 106 mm.

2. Physico – chemical analysis of the sediment sample:

The point of zero charge of the adsorbent was determined by solid addition method[19]. Ash and moisture content of the sediment sample is measured by gravimetric method. Surface area and total fluoride (F_{Total}) content of sediment sample is determined by the BET (Brunauer–Emmett–Teller) method and alkaline fusion-ion selective[20] method respectively.

3. Adsorption – desorption experiment:

Batch experiments were carried out in 100 ml conical flask containing 5 mg/L NaF solution in case of adsorption and 0.02 (M) NaOH solution in case of desorption process. The effect of pH (2.0 - 10.0), sediment dose (0.1 - 1.5 g/50 ml), interaction time (20, 40, 60, 80, 120 min), initial F⁻ concentration (1.5, 3.0, 5.0, 7.0, 10.0 and 15.0 mg/L) and temperature (20, 30, 40 and 50°C) were evaluated by varying any one variable at a time and keeping the others constant. The contents (adsorbent/50ml solution) were kept for constant shaking (at 150 rpm) in a magnetic stirrer (Remi 5MLH). The experiment was carried out in a closed system i.e., utilizing closed plastic bottles which did not allow interaction with atmospheric gases (such as CO_2) Thereafter the solution was filtered and analysed for F⁻ (Ion – selective electrode). Outcomes of the experimental data were kinetically approved by applying various isotherms (Langmuir, Freundlich and Temkin)[19] and kinetics (Pseudo-first order, pseudo-second order, intra particle diffusion model)[19].

Results and discussion

1. Sediment chemistry:

The surface area of this sediment sample is low *i.e.,* 15 m²/g[21].The particle size of this sample is 0.2 μm. The ash content and moisture content of this sample are 0.017 % and 1.25 % respectively. Point of Zero Charge (pH_{pzc}) is important characteristics for sediment sample as they indicate the acidity/basicity of the adsorbent, type of sediment and the net surface charge of the sediment in solution. In this sample, adsorption of anion is favoured at pH (8) > pH_{pzc} (7.96) that means the surface charge is negative. Total fluoride content of the sediment sample is estimated as 412 mg/kg.

2. XRD and XRF analysis of the sediment sample:

Petrographic analysis confirms that the basic mineralogy of the aquifer sediment is dominated by the presence of quartz, muscovite, and feldspar as major minerals with biotite and some ferromagnesian minerals in minor amount. XRD analysis also highlights the presence of substantial amount of zolitic clay in sample. Major oxide (wt%) analysis reveals the dominance of SiO_2 and Al_2O_3 (65.77 wt% and 14.17 wt% respectively) followed by minor occurrences of Fe_2O_3 (3.62 wt%), K_2O (3.46 wt%) CaO (3.87 wt%) and Na_2O (1.23 wt%). Significant amount of MgO (5.10 wt%) is also noticed.

3. Interpretation of adsorption-desorption experiment

i) Effect of pH: The pH of the aqueous solution is a controlling factor in the adsorption and desorption process. As depicted in Figure 1(a), it is observed that the maximum adsorption of 54.6 % is achieved at pH 2.0.

A decrease in the extent of removal of F$^-$ ions is observed with increase in the pH of the solution. One of the reasons for better adsorption at low pH values may be attributed to large number of H$^+$ ions present at these pH values, which in turn neutralizes the negatively charged OH$^-$ ions on adsorbed surface thereby reducing hindrance to the diffusion of F$^-$ ions. At higher pH values, the reduction in adsorption may be possible due to abundance of OH$^-$ ions causing increased hindrance to diffusion of F$^-$ ions. It is observed that the surface adsorbed anions favourably in low pH range due to the presence of H$^+$ ions, whereas the surface is active for the adsorption of cations at high pH values due to the accumulation of OH$^-$ ions[22,23,24]. Thus, pH of 2.0, which gave maximum F$^-$ removal, is taken into consideration for further studies. In desorption experiment, the minimum desorption observed at low pH (pH 2.0) (98.49 %) may be due to the fact that the higher concentration and higher mobility of H$^+$ ions present favoured the preferential desorption of hydrogen ions compared to F$^-$ ions. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater F$^-$ desorption. After pH 2.0 it shows that the desorbed F$^-$ ion is gradually increased with increasing pH. The maximum desorption of F$^-$ is 99.19% is achieved at pH 10.0 [(Figure 1(b)] is taken into consideration for further studies.
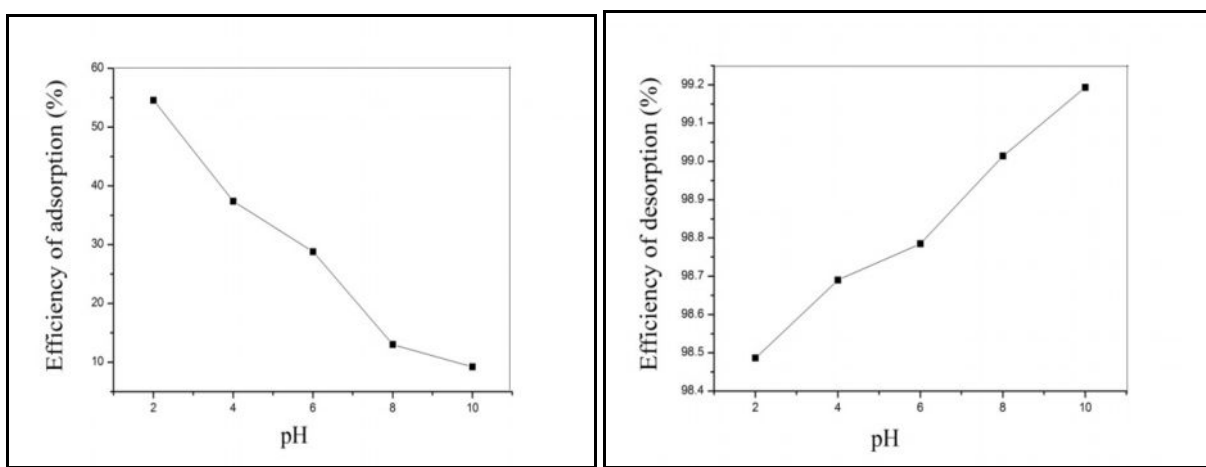
(a)   (b)

Figure 1. The effect of pH on fluoride a) adsorption (%) and b) desorption (%)
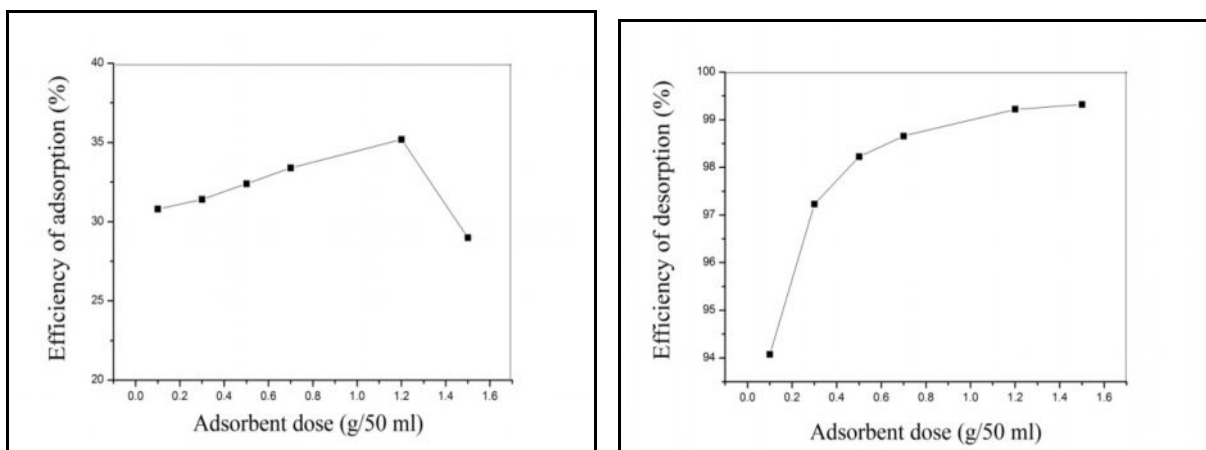
(a)   (b)

Figure 2. The effect of sediment dose on fluoride a) adsorption (%) and b) desorption (%)

ii) Effect of sediment dose: The percentage of F$^-$ removed by different dose of clay samples are represented in Figure 2. The F$^-$ adsorption increased initially with the increasing amount of the sediment. The dose of sediment having the optimum F$^-$ removal efficiency is found to be 1.2 g in adsorption (35.2 %) [(Figure 2(a)] and the efficiency of desorbed F$^-$ is 1.5 g (Figure 2(b)) in desorption experiment. This may be due to agglomeration of exposed sites. The F$^-$ removal efficiency and the efficiency of desorption are simultaneous increase with increasing sediment dose is due to the increase in surface area, and hence more active site is

available for the adsorption of F⁻. But in adsorption, after applying the dose of 1.2 g the efficiency of F⁻ removal is decreased. The best dose of 1.2 g and 1.5 g in sorption-desorption experiment are selected for further studies.

iii) Effect of interaction time: Figure 3 shows that the progression of adsorption reaction and the percentage removal of F⁻ for different interaction times. In adsorption experiment [Figure 3(a)] found that the removal of F⁻ ions decreases with increase in interaction time. In case of desorption, the percentage of F⁻ removal initially decreased at slowly, but after 60 min showed a gradually decreased. Decreased extent of sorption-desorption, particularly towards the end of experiment, indicates the possible monolayer of F⁻ ions on the outer surface, pores of the sediments and pore diffusion onto inner surface of particles through the film due to continuous mixing maintained during the experiment[24]. In the present case, 55.2 % and 99.28 % removal and desorption of F⁻ ions [Figure 3(b)] are maximum at 20 min and hence considered for further study.
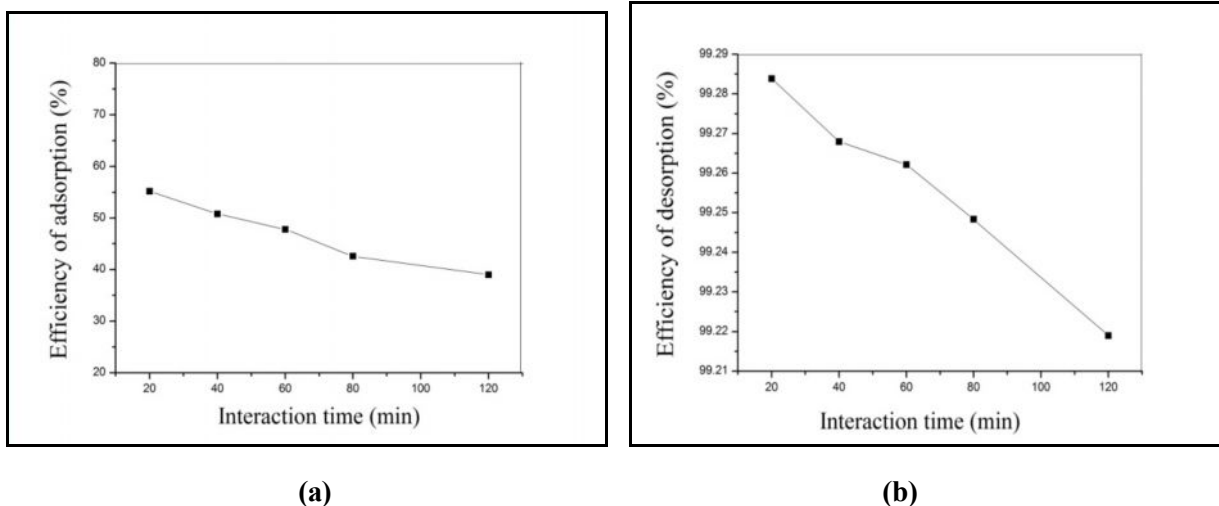

| (a) | (b) |

Figure 3. The effect of interaction time on fluoride a) adsorption (%) and b) desorption (%)
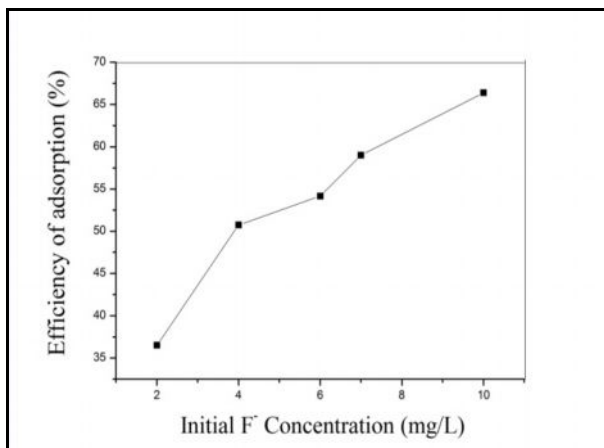

Figure 4. The effect of initial fluoride concentration on adsorption (%)

iv) Effect of initial fluoride concentration: The present experiment shows that the percentage removal of F⁻ ion increases with increase in initial F⁻ ion concentration (Figure 4). In adsorption experiment, the percentage removal of F⁻ is observed to be 36.5 % at 2 mg/L. The removal of F⁻ is gradually increased with increasing F⁻ concentration. This is probably due to the fact that for a fixed aquifer mass, the total available adsorption sites are limited. The result shows that the maximum removal of F⁻ ion in 10 mg/L.

v) Effect of temperature: The temperature graph shows that removal of F⁻ ion is decreased with increasing temperatures in adsorption experiment [Figure 5(a)] whereas in desorption, percentage of F⁻ ion is increased with increasing temperatures [Figure 5(b)]. The maximum removal of F⁻ is 61.2 % at 20°C and the minimum is 49 % at 50°C. The decrease in the percentage of F⁻ removal at higher temperatures confirms the

exothermic nature of the process. In desorption experiment the maximum and minimum efficiency of F$^-$ are 99.42 % and 99.30 % at 50°C and 20°C, respectively.
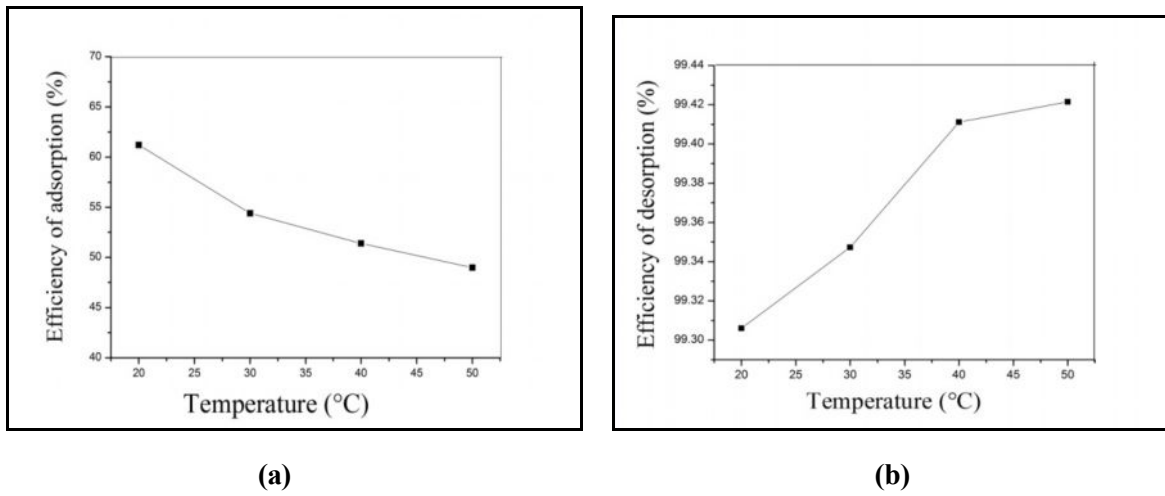

(a)   (b)

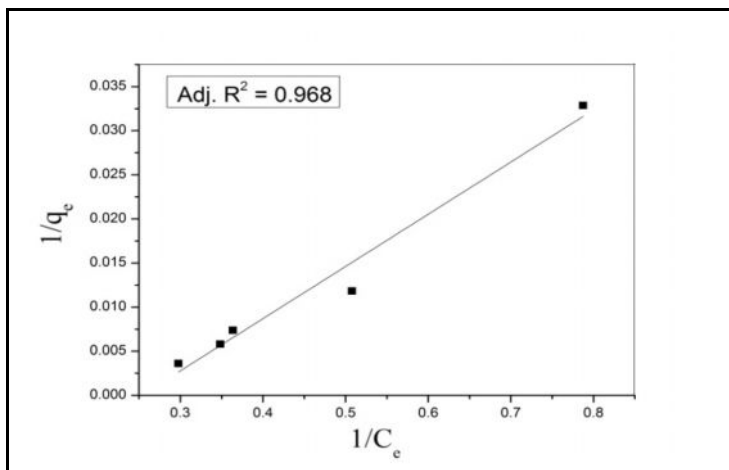**Figure 5. The effect of temperature on fluoride a) adsorption (%) and b) desorption (%)**

Figure 6. Langmuir isotherm for fluoride ion adsorption

4. Sorption mechanism

Table 1. Langmuir, Freundlich and Temkin isotherm constants for fluoride adsorption

Adsorption	Langmuir	R^2	K_L	Freundlich	R^2	K_f	1/n	Temkin	R^2	B	A
		0.968	-3.95		0.977	18.29	2.15		0.773	219.18	0.82

Langmuir, Freundlich and Temkin isotherms are plotted to provide deep insight to the adsorption of F$^-$ on sediment samples. The effect of Langmuir isotherm shape can be used to predict whether an adsorption system is 'favorable' or 'unfavorable' (Figure 6). The equilibrium parameter indicates (if $R_L > 1$, isotherm is Unfavorable; $R_L = 1$, Linear; $0 < R_L < 1$, Favorable; $R_L = 0$, Irreversible) the nature of isotherm[25]. In the present work, the quilibrium parameter which value is not come in range, so it is clear that the adsorption system is unfavourable. The Freundlich model (Figure 7) is based on the sorption which takes place on a heterogeneous phase. In the present system, a cooperative isotherm is associated where the marginal sorption energy increases with increasing surface concentration[26]. Freundlich model does not provide a conclusive evidence for the F$^-$ sorption mechanism; it provides an indirect evidence for site heterogeneity and/or surface heterogeneity.

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Laboratory scale adsorption experiment reveals good agreement with Freundlich isotherm ($R^2 = 0.977$).Temkin adsorption (Figure 8) isotherm, which considers the chemisorptions of an adsorbate onto the adsorbent, fitted not satisfactorily with correlation coefficients ($R^2 > 0.773$) (Table 1).
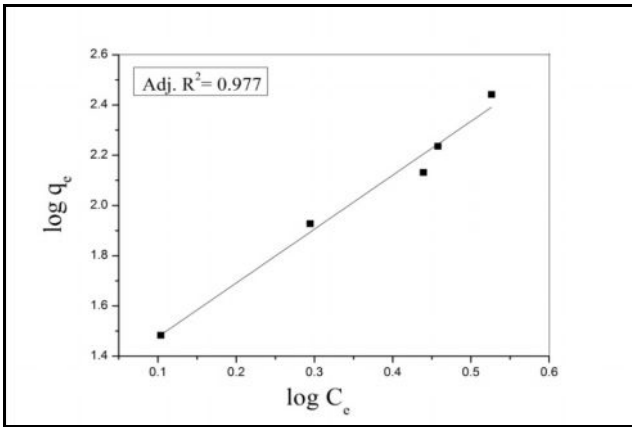

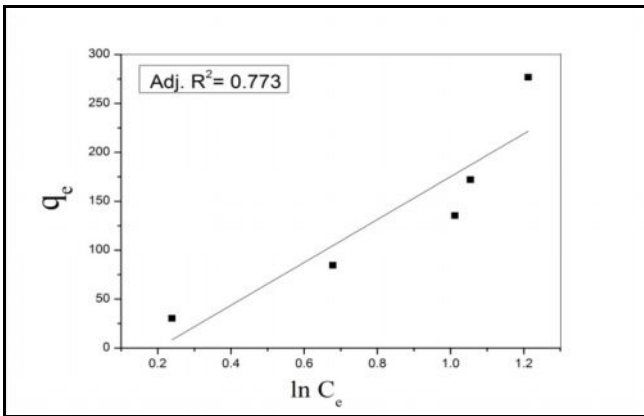**Figure 7. Freundlich isotherm for fluoride ion adsorption**

Figure 8. Temkin isotherm for Fluoride ion adsorption
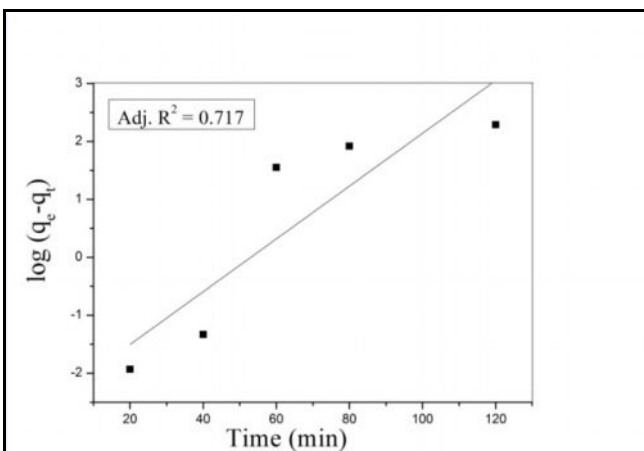
5. Kinetics analysis

Figure 9. Pseudo-first order model for adsorption

In order to investigate the controlling mechanism of adsorption – desorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order and intra-particle diffusion model equations are applied to model the kinetics of F^- adsorption onto clay samples. The first-order equation (Figure 9) of Lagergren does not fit well and is generally applicable over the initial stage of adsorption

processes[27,28]. If second-order kinetics (Figure 10) is applicable, the graph shows a linear relationship. This procedure is more likely to predict the behaviour over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step[27], which may involve valency forces through sharing or exchange of electrons between sediment and F[-] solution. Intra-particle diffusion model (Figure 11) should yield a straight line with a positive intercept for intra particle diffusion controlled adsorption process. The intercept (Table 2) gives an idea of the thickness of the boundary layer *i.e.,* the larger the intercept, the greater the boundary layer effect[29]. The kinetic study showed that a pseudo-second order models provided a better correlation ($R^2 = 0.992$) of the experimental data in comparison with the pseudo-first order model and intra-particle diffusion model.
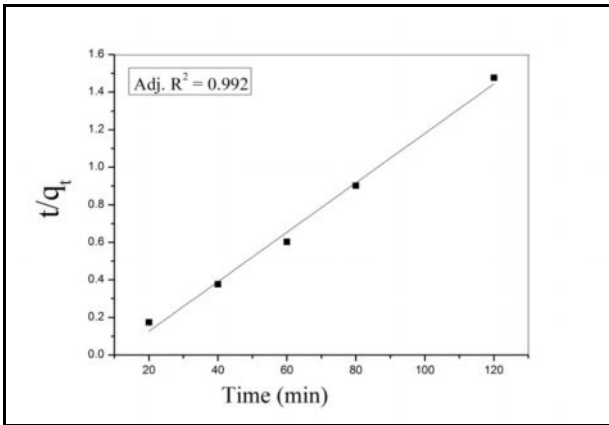

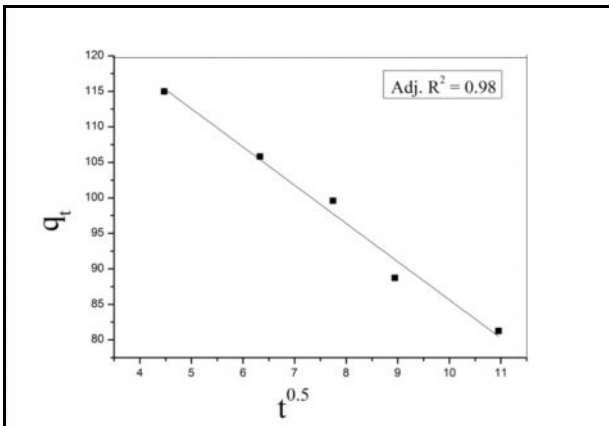**Figure 10. Pseudo-second order model for adsorption**

Figure 11. Intra-particle diffusion model for adsorption

Table 2. Parameters of Kinetic models

Adsorption		K_1 (min^{-1})	q_e(mg/ g)	R^2		K_2 (g mg^{1}min^{-1})	q_e(mg/ g)	R^2		Ki (g mg1min-1)	I	R^2
	Pseudo – first order	-0.105	0.0039	0.717	Pseudo -second order	-42117.93	75.87	0.992	Intra –particle diffusion	-5.38	139.46	0.98

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Table 3. Kinetics and thermodynamic parameters at different temperatures

Temperature (K)	Adsorption		
	$\Delta G°$	$\Delta H°$	$\Delta S°$
293	-1120.56	-12,735.64	-40.06
303	-453.45	-12,735.64	-40.06
313	-156.14	-12,735.64	-40.06
323	107.42	-12,735.64	-40.06

The effect of temperature on adsorption of F^- by sediment can be explained on the basis of thermodynamic parameters, *i.e.,* change in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$). The negative value of $\Delta G°$ indicates the feasibility of the processes (Table 3) and the spontaneous nature of F^- adsorption on sediment sample whereas the positive value of $\Delta G°$ at all temperature indicates that the non-spontaneous nature of F^- adsorption and this is an endergonic process. From the negative value of $\Delta H°$ suggests that the adsorption phenomenon is exothermic. The negative value of $\Delta S°$ reflects that no significant change occurs in the internal structure of sediment samples during the adsorption of F^-.

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