



Fluoride Ion Leaching Kinetics for Alkaline Soils of Indian Origin

S. Saxena^{1*} and A. Rani¹

¹Department of Chemistry, Maa Bharti P.G. College, Kota, Rajasthan, India.

Authors' contributions

This work was carried out in collaboration between two authors. Author SS designed the study, literature search, collected soil samples, preparation of soil column & conduct all experimental works, wrote the protocol and wrote the first draft of the manuscript. Author AR managed the interpretation of results and analyses of the study. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aims: The present research study describes leaching kinetics of F^- by loading NaF on undisturbed vertical soil column of the soil collected from Sambhar region of Rajasthan, India.

Place of Study: Government College Kota, University of Kota, Kota, Rajasthan, India.

Methodology: Alkaline soil (pH=8.2) had been collected from Sambhar region of Rajasthan, India and was dried in open air in sunlight. Dried soil was sieved for uniform particle size. The leaching kinetics of NaF has been studied by determining the fluoride concentrations in the leachate with time. Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB.

Results: Linear relationship is established between the concentrations of leachable fluoride $[F^-]$, and initial rate of leaching (LR_{obs}). $[F^-]_i$ and LR_{obs} are found to decrease with increase in Na^+ and Ca^{2+} levels of extractant, while an increase has been observed with increase in temperature and OH^- ions. While viewing the affect of OH^- ions, the effect of its accompanying cation was also investigated which indicated that maximum $[F^-]_i$ are resulted with addition of NH_4OH in percolating water and minimum with addition of KOH. Total leachable F was found to be unaffected by incubation time.

Conclusion: On the basis of the results, it is concluded that in alkaline soils, fluoride leaching will increase with increase in added NaF salts. An increase in Ca^{2+} levels of

*Corresponding author: E-mail: shwetaxena1911@gmail.com;

extractant has decreased $[F^-]_i$ and LR_{obs} . An increase in Na^+ level of extractant, some of the unleachable fluoride converts into leachable form as $[F^-]_{extra}$. The result of the study is of great significance for developing various mathematical models for salt transport processes in alkaline soil preferable in Sambhar region of Rajasthan and elsewhere in the world.

Keywords: First order kinetic model; fluoride; ion exchange; leaching kinetics; TISAB; pore volume; saturated flow; alkaline soil.

1. INTRODUCTION

Fluoride content in water depends not only on geo-chemical background of the area and climatological factors such as hydrological conditions, land forms, rainfall pattern and evaporation rate but also on the adsorption and leaching of fluoride in soil [1]. The adsorption and leaching processes directly affect fluoride migration and exchange from soil to water. In soil, some of the fluorides get immobilized, taken up by the plants and a part is also carried by the percolating water. All the processes occur simultaneously. Several studies [2] have been conducted to determine whether fluoride in rainwater was derived from anthropogenic emissions and natural sources such as sea salt cycling. A strong correlation between fluoride and sodium concentration in precipitation samples collected from marine, coastal and inland sites in India has been reported [3].

The occurrence of high F^- , a ubiquitous micro pollutant in groundwater and the risk for fluorosis associated with use of such water for human consumption is one of those environmental hazards faced worldwide. At present approximately 29 countries are reported to be affected with severe fluorosis [4,5]. Out of India's 32 states, 17 have been identified as endemic areas for fluorosis with an estimated 25 million people impacted and another 66 million at risk according to a recent survey [6]. In groundwater fluoride contaminates mainly due to leaching from fluoride rich minerals such as fluor spar CaF_2 , cryolite (Na_3AlF_6), fluoroapatite ($Ca_5F(PO_4)_3$), topaz [$Al_2SiO_4(OH)_2$], sellaite (MgF_2), villianite (NaF). Due to high solubility of NaF , it readily gets adsorbed in human body and hardly after few minutes of its intake plasma F^- concentration rises generating toxicity.

However, besides geochemical background of area and climatological factors leaching and migration depends on nature of leaching salt also. Sambhar region in Rajasthan, India is reported to have groundwater fluoride level in the range 3 to 5 ppm [4,7]. The soil of the region is old Alluvial Alkaline with Na^+ as high as 3840 meq/lit with pH 8.2. Most of the inorganic salts are either complexed with Fe and Al or remain with soluble ionic form in soil water. At the pH of soil > 7.0 under the alkaline environment, possibility of migration of soluble fluoride to the groundwater is most prominent at all temperature.

In our experimental soil (pH 8.2), the excessive amount of exchangeable Na^+ and K^+ are present naturally hydrolysed to a much greater extent than Ca^{2+} and Mg^{2+} (which are held tightly in the soil), it was interesting to investigate the chemistry of F^- leaching in this soil environment. The soil properties depicts excessive amount of Na^+ ions in comparison to Ca^{2+} and Mg^{2+} which shows that level of exchangeable sodium is high in comparison to that of Ca^{2+} and Mg^{2+} .

The present research study describes leaching kinetics of F^- by loading NaF on undisturbed vertical soil column of the soil collected from Sambhar region of Rajasthan and compared using various kinetic models. Effect of temperature, water filled porosity of the soil, OH^- ions and its accompanied cation, Ca^{2+} hardness and Na levels of percolating water etc have been investigated in detail on the total leached F^- levels as well as on initial leaching rates.

The flow method for studying leaching kinetics in saturated flow conditions as desorbed species has its own obvious importance over other kinetic methods i.e. mixed batch [8], infinite sink [9] in addition to its being pioneer attempt for studying leaching of $[F^-]$ as literature has cited leaching studies of Cl^- , SO_4^{2-} , PO_4^{3-} only [10].

2. MATERIALS AND METHODS

Alkaline soil (pH=8.2) had been collected from Sambhar region of Rajasthan, India and was dried in open air in sunlight. Dried soil was sieved for uniform particle size. The physico chemical properties of the soil used in columns are given in Table 1.1.

Table 1.1 Some physico-chemical characteristics of the column soil

Soil parameters	Value
pH	8.2
ECE	4 dsm ⁻¹
OC	1.17 %
Na ⁺	3840 meq/l
Ca ²⁺	5 meq/l
Mg ²⁺	5 meq/l
Colour	Light Grey
Bulk Density	1.48 gcm ⁻³
Type	Loamy sand
Sand %	21.9%
Silt %	10.7%
Clay %	6.8%

The leaching kinetics of NaF has been studied by determining the fluoride concentrations in the leachate with time as reported earlier [11]. Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB [12].

2.1 Procedure of Leaching Studies

Columns of soil were prepared surrounded by glass jacket of continuously flowing thermostated water. 60 g soil of pH 8.2 and of particle size ($53 > r$) was gently packed at water filled porosity $0.315 \text{ cm}^3 \text{ cm}^{-3}$. The leachate's pore volume was determined using equation (2) [13].

$$Pv = \frac{q't}{V} \quad (2)$$

where

- q' =Volume of effluent collected per unit time i.e. flow rate $\text{cm}^3 \text{ h}^{-1}$
- t =Time that has elapsed since the slug was introduced
- =water filled porosity $\text{cm}^3 \text{ cm}^{-3}$
- V =Total volume of soil column

The experimental setup of column leaching study is shown through schematic diagram at Fig. 1.0.

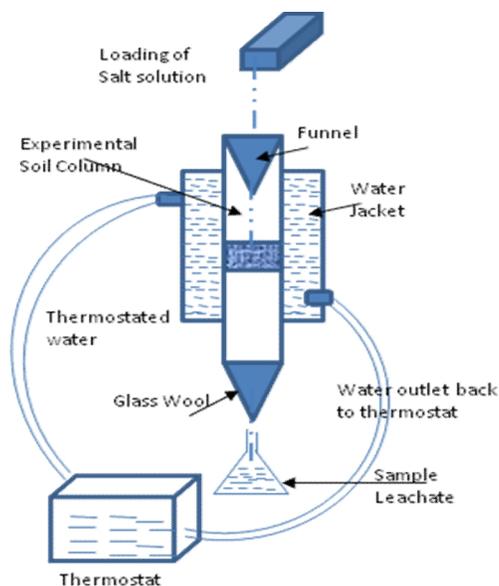


Fig. 1.0 Schematic diagram of column leaching

The flow rate of extractant was found constant (2 ± 0.5 ml/10 min). A fixed volume of aqueous salt solution (slug) with desired anion concentration (NaF) was added at the top of the soil column in each experiment. Salt solution was allowed to get adsorbed uniformly in the column for 24 hrs, after which the columns was continuously leached with de-ionized water or with other extractant as per requirement of the study. The leaching was carried out till the soluble anions were completely removed.

After completely removing the soluble ions the column soil was transferred into the beaker in a known volume of extractant. This salt solution was stirred for 2 hrs. The ion concentration was further determined in the filtrate of the soil suspension to ensure the complete removal of soluble ions from the soil in the column. The total leachable concentration was taken equal to the total leachable concentration present initially during leaching (i.e. concentration $t=0$). During each kinetic run the concentration of ions were determined in leachate collected periodically at an interval of 2 min. The treatment of result obtained in leaching studies is based on calculations of initial leaching rates as well as on applications of various kinetic models for establishing the nature of leaching kinetics of water soluble fluoride salt.

3. RESULTS AND DISCUSSION

3.1 Nomenclature

The concentration terms used for presenting the analytical results are:

$[F^-]_s$	= Leachable fluoride present in column soil, 210 mg/kg
$[F^-]_{ad}$	= F^- concentration introduced in the soil column
$C_o = [F^-]_i$	= Total leachable content present initially
$[F^-]_{complex}$	= Complexed fluoride i.e. F^- concentration retained in column
i.e. $[F^-]_{complex}$	= $\{[F^-]_s + [F^-]_{ad}\} - [F^-]_i$ When $\{[F^-]_s + [F^-]_{ad}\} \geq [F^-]_i$
$[F^-]_{extra}$	= Concentration of unleachable fluoride converting into leachable fluoride
	= $[F^-]_i - \{[F^-]_s + [F^-]_{ad}\}$ When $\{[F^-]_s + [F^-]_{ad}\} < [F^-]_i$
$C_t = [F^-]_t$	= Leached concentration at time 't'
$C_o - C_t = [F^-]_l$	= $[F^-]_i - [F^-]_t$
	= Leachable concentration remaining at time 't'
LR_{obs}	= Leaching rate

3.2 Leaching Rate Profiles

Initial rate of leaching, LR_{obs} represents the rate of change in leachable concentration with time. LR_{obs} values are obtained from the initial slopes of the plots between $[F^-]_i$ and time as shown in Fig. 1.1.

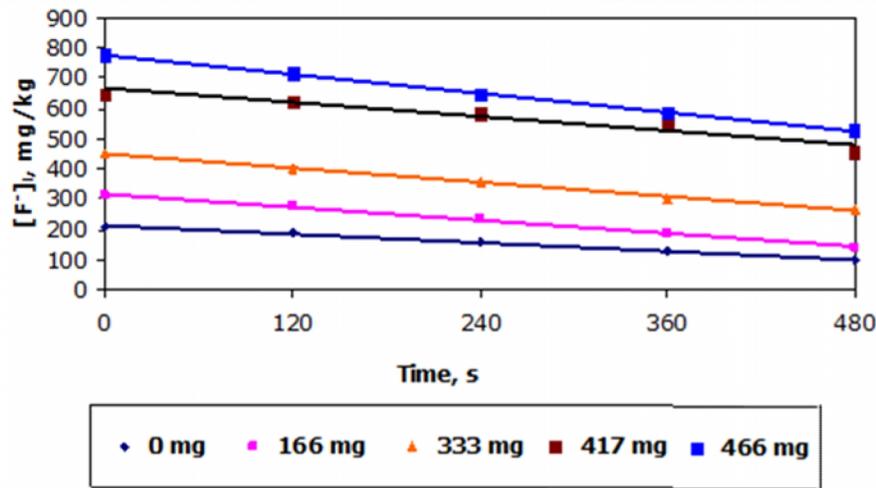


Fig. 1.1 Initial leaching rate profiles for F^- leaching for added salt NaF at 30°C.
Soil= 30 g, = 0.315 cm³ cm⁻³

3.3 Dependence of LR_{obs} on $[F^-]_i$

On increasing $[F^-]_i$ values, the LR_{obs} values seem to increase linearly (Fig. 1.2).

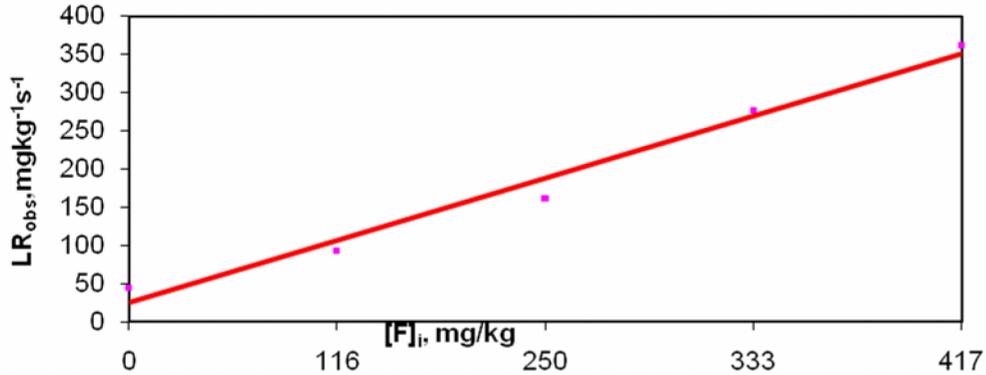


Fig. 1.2 Variation of LR_{obs} with $[F^-]_i$ for F^- leaching during NaF addition at 30°C. Soil=30g, $\rho=0.315 \text{ cm}^3 \text{ cm}^{-3}$.

To estimate fluoride leaching rates, the fluoride leaching rates can be fitted in following rate law equation (5):

$$LR_{obs} = k [F^-]_i^n + C \quad (5)$$

Where C is constant depending upon amount of naturally present leachable fluoride in the soil.

Table 1.2 The values of rate constant (k), order (n) and correlation parameters (r^2 and SEE) for F^- leaching during NaF addition

Parameter	NaF
$10^3 k$	4.14
n	1
r^2	0.99
SEE	0.26
C	35

Unit of 'k' is sec^{-1}

From the Log-Log plots of $[F^-]_i$ vs LR_{obs} , values of k and n are calculated as $4.14 \times 10^{-3} \text{ sec}^{-1}$ and 1.0 respectively.

Our experimental soil is rich in water soluble fluoride (210 mg/kg), however all the adsorption site available for fluoride are not saturated, a portion of the further added fluoride is adsorbed in the column. An order of one with respect to $[F^-]_i$ for salt proved that rate of $[F^-]$ leaching depends only upon the concentration of the total soluble fluoride available for leaching and equilibrium between the ionic and fixed fluoride is achieved very fast. In some previous studies, a fractional order < 1.0 is obtained for Cl^- and SO_4^{2-} and >1.0 for phosphate leaching in clay loam soil of pH 8.2.

3.4 Effect of Temperature

An increase in $[F]_i$ and LR_{obs} is observed with increase in temperature at fixed added concentration of NaF salt. From Arrhenius plot (Fig. 1.3) i.e. $\log k$ Vs $1/T$, the value of activation energy for fluoride releasing is determined. The activation energy is calculated to be $93.41 \pm 0.80 \text{ kJmole}^{-1}$.

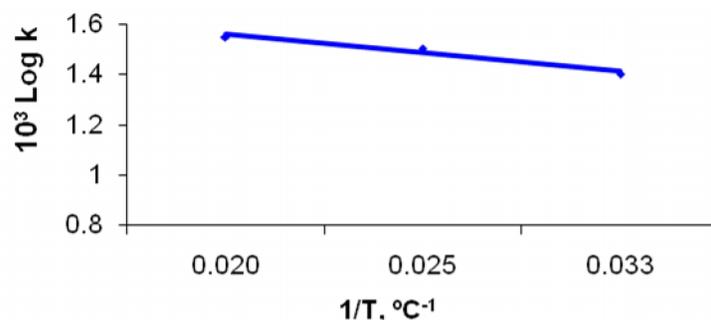


Fig. 1.3 Arrhenius plot for the determination of activation energy of F^- leaching for NaF added salts. Soil = 30 g. Soil particle size = 500 μ r 250, $\rho = 0.315 \text{ cm}^3 \text{ cm}^{-3}$

An increase in temperature results in higher leaching rates giving $93.41 \pm 0.80 \text{ kJmole}^{-1}$ values of activation energy indicating higher mass transfer due to increase in solubility rather than ion-exchange equilibrium involved in leaching specially in the present case.

At higher column soil temperature, increase can be assigned to increase in rate of solubility of salts which prevents the adsorption of ions on to soil reactive sites [14].

3.5 Effect of Hardness (Ca^{2+}) of Extractant

$[F]_i$ and LR_{obs} are found to decrease with increase in Ca^{2+} level of extractant as shown in Fig. 1.4.

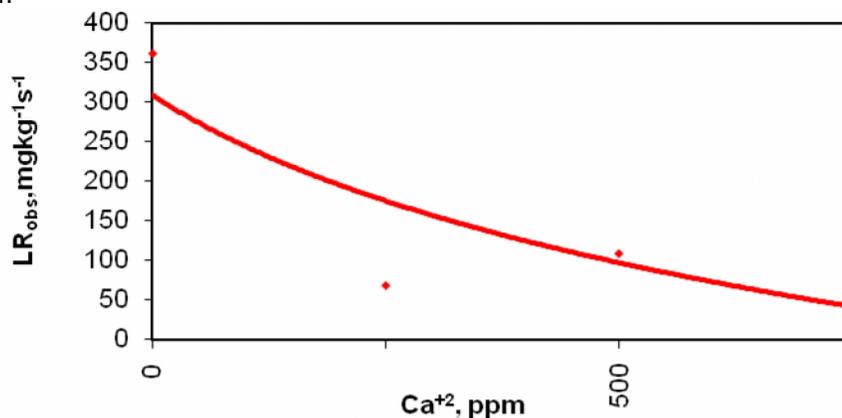


Fig. 1.4 Change in LR_{obs} with increase in Ca^{2+} concentration of extractant for F^- leaching at different added salts at 30°C . $[F]_{ad} = 466 \text{ mg/kg}$ for NaF, $[F]_{ad} = 166 \text{ mg/kg}$ Soil = 30 g

The reason for decrease in $[F^-]_i$ and LR_{obs} with rise in $CaCO_3$ content of percolating water may be due to possible precipitation of fluorite CaF_2 and fluorapatite $[Ca_5(PO_4)_3F]$ in the column [15,16]. Carbonates and bi carbonates are also reported to reduce the ionic fluoride from soil water [17].

3.6 Effect of Sodium Level of Extractant

To witness the role of Na ions present in irrigation water on leaching pattern of fluoride, Na level of extractant was varied detailed results are presented in Fig. 1.5.

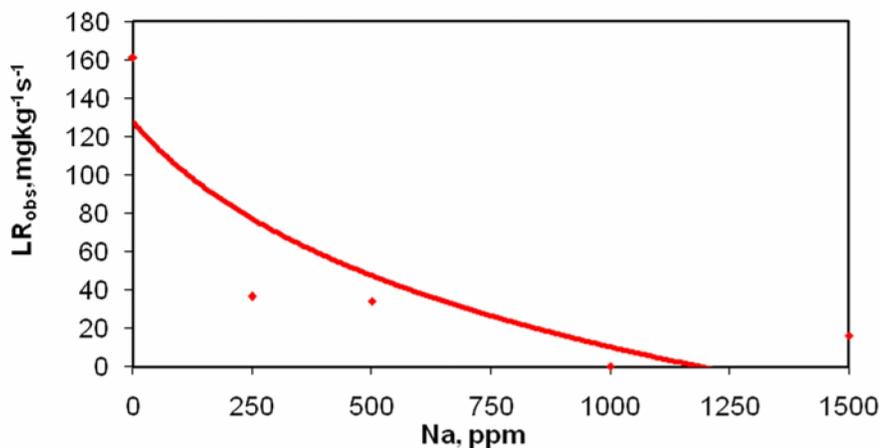


Fig. 1.5 Change in LR_{obs} with Na concentration for F^- leaching for different concentration of sodium fluoride salts at 30°C. NaF: $[F^-]_{ad} = 333\ mg/kg$

It is surprising that an increase in Na levels in extractant water has decreased $[F^-]_i$, whereas several previous studies have positively correlated F^- [18] with Na. It seems that in alkaline saline soils, sodium in extractant water has exchanged precipitated Ca^{2+} which subsequently is converted into insoluble CaF_2 lowering the soil solution F^- concentration. In an earlier F^- adsorption study also, when a sodic silt loam soil was irrigated with high NaCl, high F^- geothermal well water, CaF_2 was precipitated restricting the F^- leaching [19].

3.7 Effect of Incubation Time

The results of change in incubation time have shown no significant effect of time on total leachable fluoride. This does not exclude possibility of increased fluoride adsorption with time or with the firmness of the sink between soil and fluoride as observed by [20], but it shows that prolonged contact between soil and fluoride will not affect the capacity of percolating water to extract fluoride at least for the studied soil. Evidences from literature also support our results as during acid ammonium oxalate extraction of fluoride, F- recovery was unaffected by incubation time [21]. However a study of fluoride mobility in entisol has shown decrease in diffusion mobility of F- with rise in incubation period [12].

3.8 Effect of OH⁻ Ions

From Table 1.3 it is evident that $[F^-]_i$ and LR_{obs} are found to increase with the increase in pH levels of extractant. The order of increase in $[F^-]_i$ and LR_{obs} is found $NH_4OH > NaOH > KOH$.

Table 1.3 Change in $[F^-]_t$, $[F^-]_i$ and $[F^-]_j$ with time for F⁻ leaching during NaF addition at different pH levels of the extractant at 30°C. $[F^-]_{ad} = 166 \text{ mg/kg}$, Soil = 30 g, $\rho = 0.315 \text{ cm}^3 \text{ cm}^{-3}$

Hydroxides	NaOH		KOH		NH ₄ OH	
	10.5	12.5	10.5	12.5	10.5	12.5
pH	10.5	12.5	10.5	12.5	10.5	12.5
Time	$[F^-]_t$	$[F^-]_i$	$[F^-]_t$	$[F^-]_i$	$[F^-]_t$	$[F^-]_i$
0	0	300	0	473	0	433
120	1	299	17	456	3	418
240	3	297	33	440	10	373
360	17	283	50	423	20	345
480	43	257	77	396	33	314
600	77	223	107	366	50	268
720	93	207	130	343	67	238
840	110	190	157	316	83	208
$[F^-]_i$	300	473	250	317	383	433
$LR_{obs}, \text{mgkg}^{-1}\text{s}^{-1}$	44.01	89.63	25.63	24.82	99.38	121.18

$[F^-]_t$, $[F^-]_i$ and $[F^-]_j$ are in mg/kg

As the radii of F⁻ and OH⁻ ions are comparable, an exchange of OH⁻-F⁻ is inevitable which showed increased fluoride leaching with increase in OH⁻ concentrations. Surprisingly the cation attached to OH⁻ ion which affected F⁻ leaching significantly, the maximum being with NH₄OH and minimum with KOH. NH₄⁺ ions which can carry at least 4 F⁻ ion through H-F bond [22] result in highest $[F^-]_i$ and LR_{obs} value in our experiment.

It seems that replacement of OH⁻ ion is more in case of NaOH than KOH as the lattice energy of KOH is more because of which availability of free OH⁻ ions are less in KOH in comparison to NaOH.

Unlike other soluble ions, F⁻ is not leached much from naturally salinized salt affected soil rather it is redistributed within the soil profile. The adsorption of F⁻ to soil increases with decrease in soil pH in acidic soil while in most of the alkaline soil F⁻ is replaced by OH⁻ ion producing high leachable concentration of ionic fluoride [23]. Thus the leaching rate of F⁻ is always found higher in an alkaline soil. The maximum leaching is observed when NH₄OH is added in percolating water because of H-F bonding with NH₄⁺ which can carry more number of F⁻ ions (at least 4) with single NH₄⁺ ion resulting in highest $[F^-]_i$ and LR_{obs} values. It seems that replacement of OH⁻ ion is more in case of NaOH than KOH as the lattice energy of KOH is more because of which availability of free OH⁻ ions are less in KOH in comparison to NaOH.

The maximum leaching occurs on adding NH₄OH and minimum with KOH. Some earlier studies on adsorption and desorption of F⁻ on soil of China interpreted as competing sorption of OH⁻ in soil solution replacing some F⁻ from surface of soil colloids resulting in increase in leaching of F⁻. The leaching rate of F⁻ was found higher in alkaline soil than acidic. In some groundwater quality assessment studies F⁻ was positively correlated with pH [18].

3.9 Application to the Kinetic Models

To describe F^- leaching kinetics, several kinetic models were tried and it was observed that First order kinetic model [24,25] is found to be most suitable for leaching of fluoride for NaF salt (Fig. 1.6). The concentration terms used in different equations are as follows:

$$[F^-]_i = C_0; [F^-]_t = C_t; [F^-]_i - [F^-]_t = C_0 - C_t; \ln(C_0 - C_t) = a - bt$$

Kinetic models tried are as under:

Kinetic Model	Rate Equation
Zero order kinetic model	$C_0 - C_t = a - bt$
First Order Equation	$\ln(C_0 - C_t) = a - bt$
Second Order Equation	$1/C_t = a - bt$
Parabolic Diffusion	$C_t = a - bt^{1/2}$
Elovich Equation	$C_t = a - b \ln(t)$

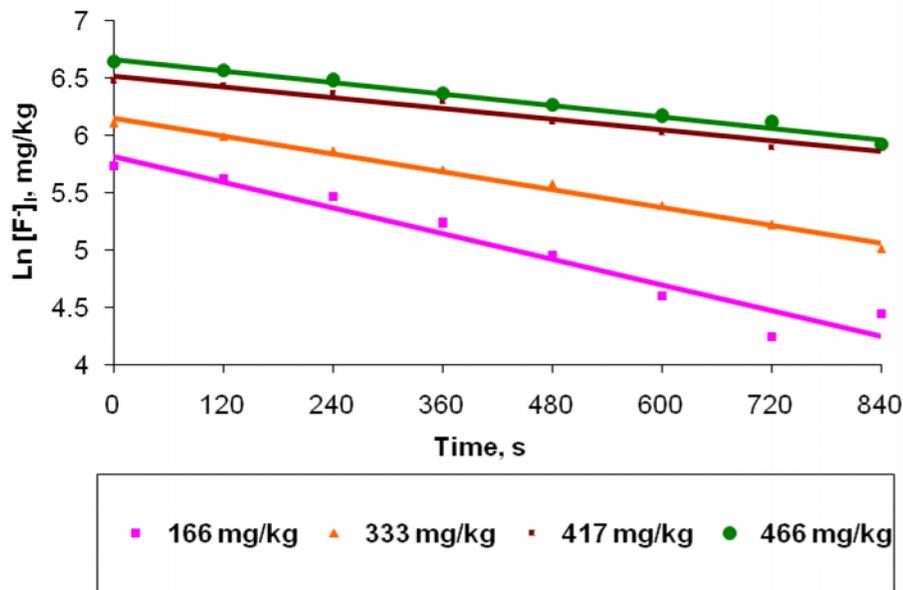


Fig. 1.6 First Order equation profile for F^- leaching during NaF addition at different $[F^-]_{ad}$ at $30^\circ C$. Soil = 30 g, $\rho = 0.315 \text{ cm}^3 \text{ cm}^{-3}$

Out of 5 different kinetic models, first order kinetic model is the best suited one. Thus the order using integrated rate equation as well as initial rate equation is identical for F^- leaching in alkaline soil, if added salt is NaF. The results of the present study can be utilized for developing F^- leaching models in fluoride endemic areas and measuring groundwater pollution due to fluoride leaching.

4. CONCLUSION

The present study throws light on the leaching behaviour of soluble ionic salt in saturated flow condition in alkaline soil and its migration to groundwater. Interesting results about the effects of various factors such as decrease in $[F^-]_i$ and LR_{obs} with increase in Na^+ and Ca^{2+} levels of the extractant and increase in the same with temperature and OH^- ion. These can be used for estimating leaching rate of F^- from contaminated soil of fluoride endemic areas and thus are of great significance for developing various mathematical models for salt transport processes in alkaline soil preferable in Sambhar region of Rajasthan and elsewhere in the world.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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