

The Leaching Kinetics of Nitrate in Soil Using Glass Column Method

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Abstract: The leaching kinetics of nitrate (NO_3^-) in agricultural ($\text{pH} = 7.2$) and non-agricultural soils ($\text{pH} = 6.8$) was studied using undisturbed glass columns method. The soils were taken from the agriculture field and barren land near Dheerkhera agricultural area, Hapur. The Sodium nitrate (NaNO_3) is used as a source of NO_3^- . Power form equations ($\text{LR}_{\text{obs}} = k_1 [\text{NO}_3^-]_i^{2.91}$ for agricultural and ($\text{LR}_{\text{obs}} = k_2 [\text{NO}_3^-]_i^{1.829}$ for non-agricultural soils have been derived for dependence of LR_{obs} on leachable concentration of NO_3^- present initially. The effects of pore volume, temperature, Ca hardness have been observed on leaching rate. Change in water filled porosity θ ($\text{cm}^3 \text{cm}^{-3}$) of the column has been found to affect LR_{obs} . The LR_{obs} is found to increase with temperature in the range $30\text{-}50^\circ\text{C}$. Experimental data fitting on various kinetic models showed first order kinetic models and parabolic diffusion to be most suited for predicting leaching rates.

Keywords: Nitrate, adsorption, leaching, glass column, first order, pore volume, BTC.

I. INTRODUCTION

Nitrogen is both an essential nutrient and a large source of pollution on the terrestrial ecosystems. Due to an important component of plant nutrients, nitrogen plays an important role in increasing crops yields and its quality [1]. Hence the nitrogen in form of Nitrate, Ammonium, or Urea (which rapidly hydrolyses to ammonium) are used to increase the crops yields. In contrast to ammonium ions, NO_3^- are not adsorbed by the negatively charged colloids that dominates most soils. Therefore nitrates ions can move downward freely with the drainage water and are thus readily leached from the soil. Such leaching losses will cause serious environmental problems [1].

Leaching is one of the most important physical processes responsible for migration of soil nutrients and pollutants. Over fertilized agricultural areas poses a threat to the ground water quality mainly because of leaching of salts through macropores along with percolating water [2]. As the water moves through the soil profile, it dissolves additional salts from the soil and transport them to subsurface and ground water [3]. The leaching rates of salts are basically the relative mobility of water along with salt movement. One of the worst consequence of leaching from polluted sites as well as from over fertilized agricultural fields during irrigation, rain events and water percolation is contamination of subsurface and ground water [4]. By using the excess of nitrogen fertilizers at the rate higher than plant uptake can increase the chance of nitrate leaching by many times [5]. Leaching of solute also depends on amount of water applied by irrigation or natural precipitation [6] and the amount, timing and species of fertilizer applied [7]. Nitrate leaching from the unsaturated zone is a complex phenomenon involving many factors such as land use practices, soil nitrogen dynamics, on-ground nitrogen loading, groundwater recharge, soil characteristics, the depth to water table [8]. Leaching may depend on macro porosity of soil [9] as well as laminar flow of water in cracks and channels found in soils [10]. Leaching also depends on salt solubility, initial water content of soil [11], pH [12], temperature, etc.

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Studies conducted in different parts of the world have shown that farmers often use amount of N fertilizers that exceed the N requirement of crops. Nitrate is soluble and negatively charged and thus has a high mobility and potential for loss from the unsaturated zone by leaching [15],[16]. Many studies showed high correlation and association between agriculture and nitrate concentration in groundwater [17],[18],[19]. The extensive use of fertilizers is considered to be a main non-point source of the nitrate [20],[21],[22] and point sources of nitrogen such as septic systems are shown to contribute to nitrate pollution of groundwater [23]. Elevated nitrate concentrations in drinking water can cause Methemoglobinemia in infants and stomach cancer in adults [2],[18]. The US Environmental Protection Agency (US EPA) has established a maximum contaminant level of 10 mg/L $\text{NO}_3^- \text{N}$. As a significant quantity of nitrogenous fertilizer can be transported through preferential flow pathway in the soil [23], [20]. The downward movement of NO_3^- in agricultural and non-agricultural soils is studied using glass column method, The Effect of Ca hardness of extractant, irrigation water quality, water filled porosity of the soil, temperature and salt concentrations have been investigated on rate of leaching of nitrate ion in soil.

(II) RELATED WORK

Literature survey revealed that studies on kinetics of leaching of various chemicals [31,34] through soils and soil mineral are rare. Most of the desorption and leaching [32, 33, 37,38] studies of nitrate give only preliminary idea about the leaching. None of them reported utilization of initial rate kinetic method for studying leaching of chemicals on columns of natural soils with continuous or restricted flow in saturated and unsaturated conditions. The present investigation has been carried out to investigate the leaching kinetics of NaNO_3 , a highly soluble NO_3^- salt present in the agricultural field. Most of the studies conducted on NO_3^- leaching are from the regions where rainfall is abundant and well distributed [26] but studies under semi arid condition are scares.

(III) MATERIALS AND METHODS

Soil samples were collected from the agricultural fields of Dheerkhera area of Hapur where crops are grown and chemical fertilizers are continuously applied during the last ten years. Non-agricultural soil samples were collected from barren lands where crops are not grown and chemical fertilizers are not applied. Soil samples were collected by digging a deep pit. Samples were collected and placed in plastic bags and labeled according to their field. Soil samples were collected 2-3 times in a month at every site during the entire study period. These samples were dried and sieved. Table 1 gives physicochemical characteristics of the soil analyzed using standard methods [27].

The leaching kinetics of NaNO_3 was studied by determining the nitrate concentrations in the leachates with time. Initial leaching rates (LR_{obs}) have been calculated using plane mirror method [29]. Nitrate was estimated using standard spectrophotometric method [27]. In this method aliquot was evaporated to dryness over a hot water bath, and 2 mL of Phenol disulphonic acid was added to it and then 5 mL Ammonium hydroxide was added to develop colour and diluted to 100 mL with deionized water. The calibration curve was obtained at 410 nm using NO_3^- solution of different concentrations. The concentration (mg L^{-1}) in leachates were converted to mg kg^{-1} in soil during kinetic work.

TABLE 1.

Some physicochemical characteristics of the soil

Properties	Non-Agricultural soil	Agricultural soil
pH	6.8	7.2
E.Ce (dS m^{-1})	0.67	0.242
Bulk density (g cm^{-3})	1.50	1.51
Colour	Brown to dark brown	Grayish black
Sp. Gravity	2.57	2.71
Texture	Clay-clay loam	Clay loam
Sand (%)	21.2	23.2
Silt (%)	26.2	43.2
Clay (%)	48	33.1

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CEC	46.01	28.8
OC (g kg ⁻¹)	6.5	6.84
Available N (kg ha ⁻¹)	232	216
Available P (kg ha ⁻¹)	17	21
Available K (kg ha ⁻¹)	291	331.2

Procedure of Leaching Studies

For studying leaching kinetics, specially designed graduated glass columns of 60 cm length and 3 cm diameter were prepared. They were surrounded by glass jacket for continuously flow of thermostatic water. To maintain the temperature constant of circulating water in glass jackets surrounding the glass column, manually fabricated thermostat with electronic relay, Beckman thermometer, mechanical stirrer and heating rod were used. 60 g soil with pH 6.8 and of known particle size ($500 \mu \geq r$) was gently packed at water filled porosity $0.34 \text{ cm}^3 \text{ cm}^{-3}$ for agriculture and $0.33 \text{ cm}^3 \text{ cm}^{-3}$ for non agriculture soil. The pore volume (P_v) [28] was determined using equation (1).

$$P_v = q t / \theta V \tag{1}$$

where

q = volume of the effluent collected per unit time *i.e.* flow rate

$$\theta = \text{water filled porosity } \text{cm}^3 \text{ cm}^{-3} = \frac{\text{Volume of water ed by dry soil}}{\text{Total volume of soil column}}$$

V = total volume of the soil column

A fixed volume of aqueous salt solution (fertilizer) was added from the top of the soil column was allowed to get adsorbed uniformly in the column for 24 h. The column was then continuously leached with deionised water till the soluble anions were completely removed. During all the kinetic runs the column length, flow rate, pH of percolating water and temperature were also kept constant in all the experiments except during temperature variation studies. Effect of temperature, pore volume, Ca hardness of extractant water were studies only in non-agricultural soil columns. The results were found to be reproducible within $\pm 10\%$.

The treatment of data is based on the calculation of the following parameters as defined below:

$[\text{NO}_3^-]_s$	=	Leachable nitrate present naturally in column soil
$[\text{NO}_3^-]_{\text{add}}$	=	Nitrate concentration introduced in the soil column as soluble NaNO_3
$[\text{NO}_3^-]_i$	=	Total leachable content present initially.
$[\text{NO}_3^-]_t$	=	Leached concentration at time 't'.
$[\text{NO}_3^-]_l$	=	$[\text{NO}_3^-]_i - [\text{NO}_3^-]_t$ = Leachable concentration remaining at time 't'.
$[\text{NO}_3^-]_{\text{ads}}$	=	$[\text{NO}_3^-]_s + [\text{NO}_3^-]_{\text{ad}} - [\text{NO}_3^-]_i$

(IV) RESULTS AND DISCUSSION

A. Total Leachable Nitrate $[\text{NO}_3^-]_i$

The soil itself has naturally leachable $[\text{NO}_3^-]_s$ in it. On adding NO_3^- from outside in the form of NaNO_3 , concentration of leachable nitrate increases, with the increase in amount of added salt. It is clear from the result of table 2 and fig.1 that $[\text{NO}_3^-]_s$ *i.e.* (leachable nitrate present naturally in soil column) are higher in agricultural soil in comparison to non- agricultural soil.

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TABLE 2.
Variation in $[NO_3^-]_i$ and LR_{obs} with $[NO_3^-]_{add}$ for $NaNO_3$ leaching in agriculture and non agriculture soil at $30^\circ C$

$[NO_3^-]_{add}$	Agricultural soil			Non-agricultural soil		
	$[NO_3^-]_i$	$[NO_3^-]_{ads}$	LR_{obs}	$[NO_3^-]_i$	$[NO_3^-]_{ads}$	LR_{obs}
0.0	84	0.0	4.48	30	0.0	.48
17.72	100	1.72	8.49	41	6.72	.96
35.44	110	9.44	13.44	50	15.44	1.536
53.16	125	12.16	18.33	64	19.16	2.52
70.88	145	9.88	23.36	74	26.88	2.94
88.6	160	12.6	31.41	84	34.6	3.76
106.6	178	12.32	45	101	35.6	4.11

LR_{obs} in $mgkg^{-1}s^{-1}$

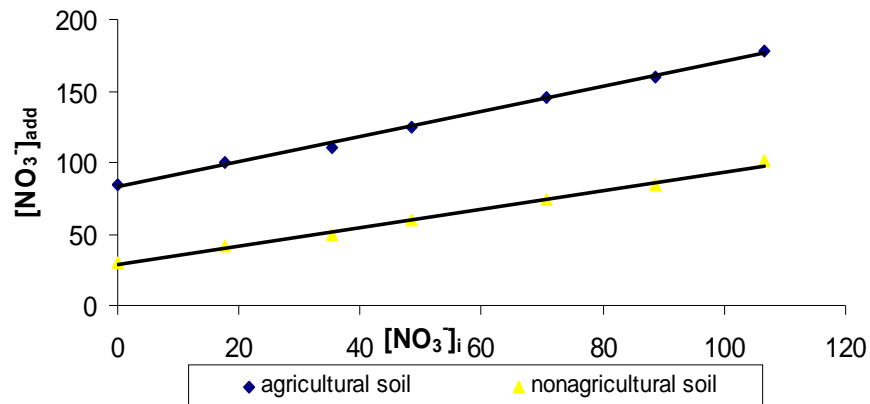


Fig.1 Variation of $[NO_3^-]_i$ with $[NO_3^-]_{add}$ for $NaNO_3$ addition at $30^\circ C$ for agricultural and nonagricultural soil

B. Leaching of $NaNO_3$

Leaching of NO_3^- ion was studied at different added concentration of $NaNO_3$ on soil columns. Amount of $NaNO_3$ was varied from 0 to 106.6 mg kg^{-1} . The flow rate of percolating water was $10 \pm 2 \text{ mL}$ per 10 minutes. The results of $NaNO_3$ leaching for variable $[NO_3^-]_i$ are given in table 2 for agriculture and non-agriculture soil. From the Figs. 2 and 3 it is clear that initial leaching is relatively fast for almost all the $[NO_3^-]_i$ in both types of soils. The LR_{obs} values are found higher in agriculture soil in comparison to non-agriculture soil for similarly added $NaNO_3$.

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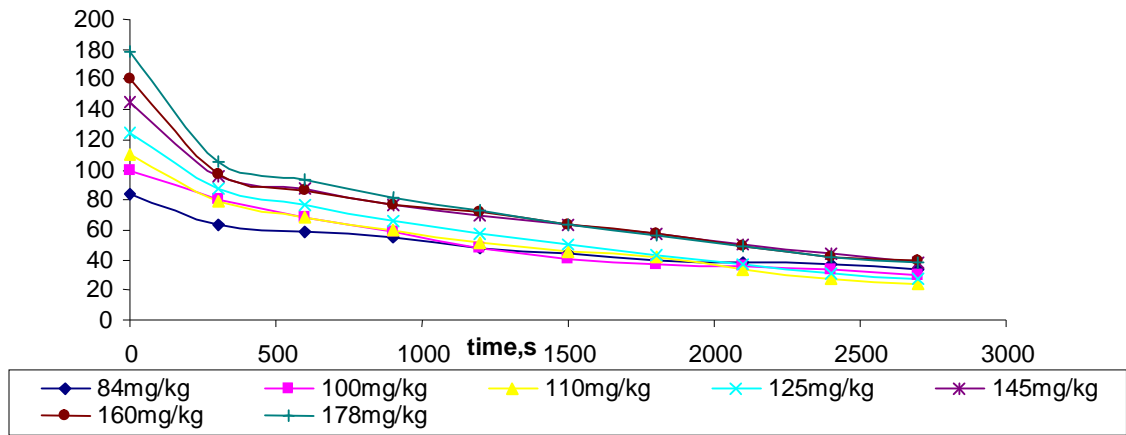


Fig.2 Leaching rate profile for NaNO₃ at different [NO₃⁻]_i at 30°C for agriculture soil

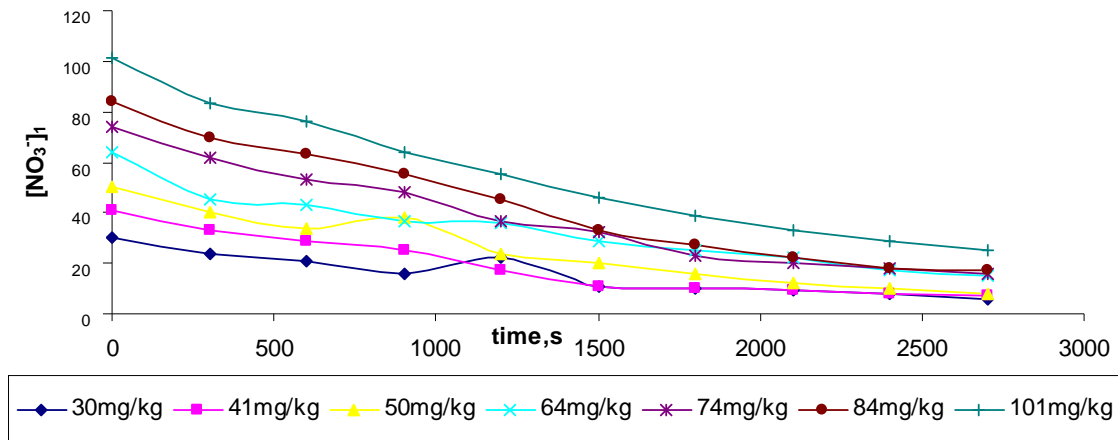


Fig.3 Leaching rate profile for NaNO₃ at different [NO₃⁻]_i for non-agricultural soil at 30°C

C. Leaching Rate Profile & Dependence of LR_{obs} on [NO₃⁻]_i

Initial rates for leaching, LR_{obs}, represents the rate of change in leachable concentrations, [NO₃⁻]₁ with time. LR_{obs} values were

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obtained from the slope of the initial rate plot using the plane mirror method by Max Latshaw[29]. It can be concluded from table 2 that with the increase of $[NO_3^-]_i$, the LR_{obs} is also increased. The log-log plot between the initial total leachable content $[NO_3^-]_i$ and the LR_{obs} for agricultural and non agricultural soil indicated a fractional order of more than one i.e. 2.91 and 1.82 respectively given in table 3. The rate laws are given for $NaNO_3$ for agricultural and non agricultural soil are

$$LR_{obs} = k_1 [NO_3^-]_i^n \quad \text{For agricultural soil}$$

$$LR_{obs} = k_2 [NO_3^-]_i^n \quad \text{For non-agricultural soil}$$

TABLE- 3

The values of rate constant (k), order (n) and correlation parameters (r^2) and SEE for leaching of $NaNO_3$ in agricultural and non-agricultural soil at 30 °C

Parameters	Agricultural soil	Parameters	Non-agricultural soil
$10^3 k_1$	0.406	$10^3 k_2$	0.108
n_1	2.91	n_2	1.829
r^2	0.980	r^2	0.975
SEE	0.120	SEE	0.0739

D. Effect of Temperature

The effect of temperature on $[NO_3^-]_i$ and LR_{obs} was studied in the range 30-50 °C at different added $[NO_3^-]_{ad}$. Results given in table 4 show that with increase in temperature, the solubility of adsorbed nitrate is increased, thus leaching is increased. Ref [36] has also given three effects of temperature on the reaction between inorganic phosphate and soil in which phosphate was present (a) in solution, (b) adsorbed in equilibrium with solution and (c) firmly held. In our experimental conditions, as the desorbed nitrate was continuously removed by the water from macro-pores through leaching, increase in temperature has increased solubility of firmly held or surfacial adsorbed nitrate remarkably, increasing equilibrium nitrate concentration in soil water giving higher LR_{obs} and $[NO_3^-]_i$ values for added nitrate salts.

The effect of temperature on $NaNO_3$ leaching was examined in detail only in non-agricultural soil by applying the Arrhenius equation i.e. $k = Ae^{-E_a/RT}$ on the rate constant data. A plot of $\log k$ vs. $1/T$ yielded a straight line. The slope of which gives activation energy E_a as 29.480 KJ mol⁻¹.

TABLE 4.

Variation of LR_{obs} with $[NO_3^-]_i$ at the different temp. for non-agricultural soil

$[NO_3^-]_{ad}$	0		17.72		35.44		53.16		70.88		88.6		106.6	
Temp. °C	$[NO_3^-]_i$	LR_{obs}	$[NO_3^-]_i$	LR_{obs}	$[NO_3^-]_i$	LR_{obs}	$[NO_3^-]_i$	LR_{obs}	$[NO_3^-]_i$	LR_{obs}	$[NO_3^-]_i$	LR_{obs}	$[NO_3^-]_i$	LR_{obs}
30	30	0.48	41	0.96	50	1.536	64	2.52	74	2.94	84	3.76	101	4.11
40	34	0.61	43	1.08	53	1.7	66	2.55	76	3.00	87	3.78	103	4.13
50	38	0.83	46	1.25	56	1.86	70	2.87	79	3.50	90	3.9	106	4.2

E. Effects of Ca^{2+} Levels of Extractant H_2O

Ca^{2+} Levels of extractant was varied from 250-1000 mg L⁻¹ by adding Ca^{2+} in the form of $CaCl_2$. $[NO_3^-]_i$ and LR_{obs} were found to decrease on increasing Ca^{2+} level of extractant water. Results are given in table 5. Addition of Ca^{++} ions in the extractant water retarded the initial rate of nitrate leaching. If irrigation water is hard it may affect the NO_3^- leaching in two possible ways.

- (1) It may change the ion-exchange capacity of the soil and (2) downwards movement of NO_3^- ion will be coupled with the hydrated Ca^{2+} . As the size of hydrated ions of Na^+ is smaller in comparison to Ca^{+2} hydrated ions, the rate of

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leaching of NaNO₃ will be retarded in presence of excessive Ca⁺² ions.

TABLE 5.
Effect of change in Ca content of extractant H₂O on NaNO₃ leaching at 30 °C

Ca ⁺⁺ (mg kg ⁻¹)	[NO ₃ ⁻] _i	L ^R _{obs}
added	(mg kg ⁻¹)	(mg kg ⁻¹ s ⁻¹)
0	50	1.536
250	45	1.35
500	38	1.20
1000	30	.980

F. BTC of leaching

Breakthrough curves obtained in this study supports previous views [35] that in undisturbed naturally structured soil only partial displacement of resident water and solute by incoming water and solute occurs. Fig. 4 gives change in relative concentration

[NO₃⁻]_t / [NO₃⁻]_i with number of pore volume, which estimates change in the volume of soil water with time participating in solute transport .Ref [35] has reported that the pore volume of the effluent depends on the flow velocity and initial **water** content θ of the soil column, but as in the present case, [13] has also studied the effect of θ on Mg leaching and showed that leaching of salt is accompanied by diffusion of adsorbed/desorbed salt in to the extractants volume present in the macroscopic pores of the soil column. Higher is the adsorption, lesser will be the effect of θ on leaching rates as shown in fig. 4

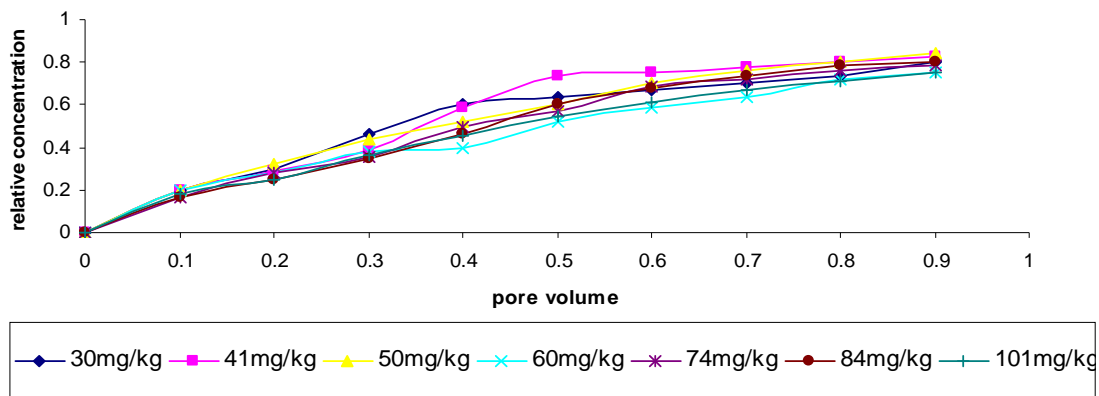


Fig. 4 Variation in relative concentration and number of pore volume at different [NO₃⁻]_i at 30 °C

G. APPLICATION OF STUDY

Most of the earlier studies on kinetics of NO₃⁻ desorption from soil found that release of NO₃⁻ deviate from zero order kinetic reaction and described better by a first order reaction [22]. Ref [36] used the framework of Freundlich equation and developed kinetic model for desorption incorporating power form equation. He explained that parameters of the models depended upon the length of the incubation period allowed, addition of solute to soil and the start of desorption further. Chien and Clayton (1980) described desorption of phosphate by modified form of Elovich equation. Power form equation used by us is different in

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the manner that it includes initial leaching rates but not the initial amount of desorbable NO_3^- . This equation is more suited to present soil conditions. Besides, experimental results were also fitted to the previously explained conventional kinetic models. Average values of slope, r^2 and SEE are given in table 6, for different concentration of $[\text{NO}_3^-]_i$ for the NO_3^- salts. It is clear from the table that first order equation (Fig. 5) and parabolic diffusion (Fig. 6) are most suitable to describe NO_3^- leaching.

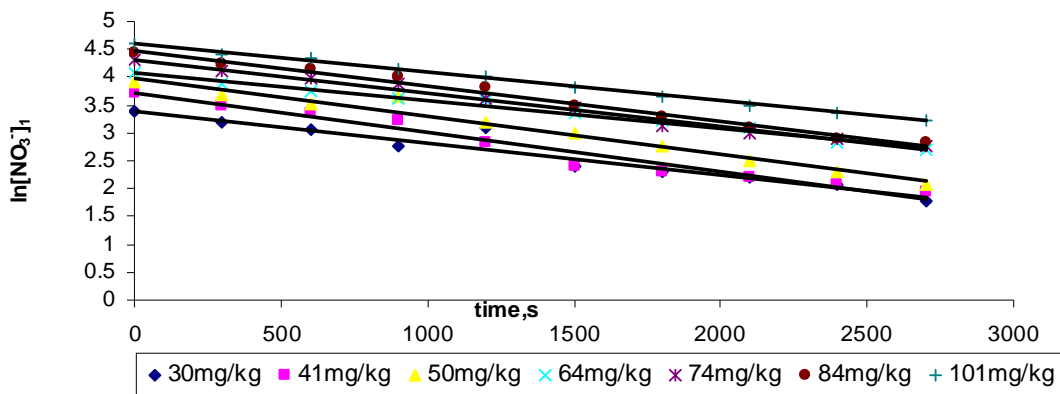


Fig. 5 First Order equation profile for the NaNO_3 leaching for non agricultural soil for different $[\text{NO}_3^-]_i$ at 30°C

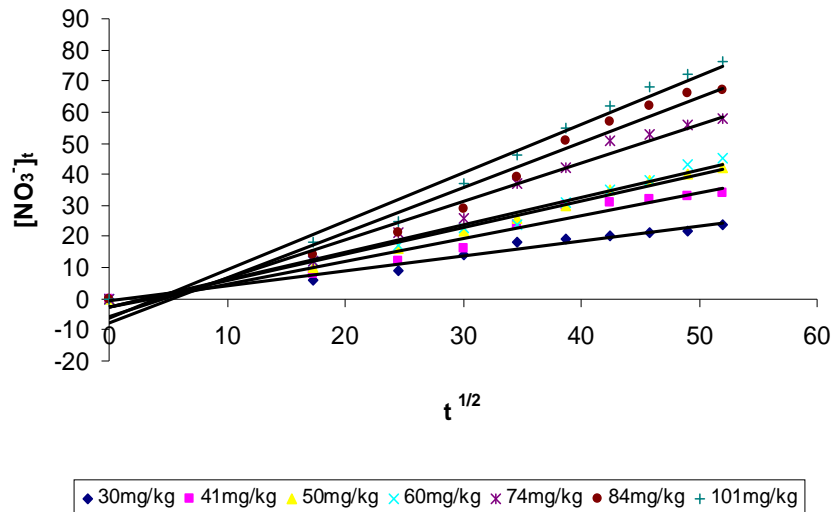


Fig. 6 Parabolic equation profile for leaching of NaNO_3 at different $[\text{NO}_3^-]_i$ at 30°C

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TABLE 6.

Coefficient of determination (r^2), standard error of estimate (SEE) and slope for graphical equations of different kinetic models applied on NaNO_3 leaching

Kinetic models— >	Zero order			First order			Parabolic diffusion		
	r^2	SLOPE	SEE	r^2	SLOPE	SEE	r^2	SLOPE	SEE
$[\text{NO}_3^-]_i$ (mg kg ⁻¹)									
30	.88	-.0084	3.897	.928	-.0006	.154	.960	.515	1.30
41	.91	-.0127	3.866	.964	-.0007	.130	.943	.833	2.52
50	.945	-.0155	3.575	.972	-.0007	.110	.996	.741	.960
64	.966	-.0155	2.804	.966	-.015	2.804	.983	.985	1.56
74	.955	-.0217	4.530	.988	-.0006	.0625	.983	1.42	2.29
84	.963	-.0256	4.772	.987	-.0006	.0691	.979	1.71	3.097
101	.964	-.027	5.072	.998	-.0005	.0217	.992	1.79	1.97

(V) CONCLUSION

This study was conducted following a multidisciplinary approach to obtain data necessary for a better representation of NO_3^- transport from the soil. It has been successfully represented the results of column study in the power form equation to represent nitrate leaching accurately. A fractional order of >1.5 and <3.0 has been observed for leaching of NaNO_3 . Results of this study showed that leachable NO_3^- is higher in agriculture soil columns in comparison to non-agricultural soil columns while adsorbed NO_3^- concentration is higher in non-agricultural soil columns. Increasing the water filled porosity does not impart any significant change in $[\text{NO}_3^-]_i$ as well as on LR_{obs} .

Several earlier studies [31], [33], [34] have given higher levels of nitrate in agricultural fields but relationship between rate of leaching with concentration of nitrate in soil were not reported in any study. This method can also be applied in the agricultural fields to know fertilizer requirement of plants as well as leaching rates below root zone.

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