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LEACHING KINETICS OF Na IN ALKALINE SOIL OF KOTA, RAJASTHAN UNDER THE INFLUENCE OF ADSORPTION-DESORPTION

DIMPLE GOYAL and ASHU RANI*

Department of Pure and Applied Chemistry, University of Kota, KOTA (Raj.) INDIA

ABSTRACT

The kinetics of leaching of sodium has been studied on undisturbed columns of alkaline soil (pH=8.2) of Kota region of Rajasthan, India. NaCl has been taken as the source of added sodium. Initial leaching rates ($LR_{obs)}$) have been calculated using Latshow method and linear power form equation ($LR_{obs} = k[Na^+]_i$) has been derived for dependence of LR_{obs} on leachable concentration of Na present initially in the column during leaching. Effect of Ca-hardness of extractant and that of temperature in the range of 20-50^0 C on $[Na^+]_i$ and LR_{obs} was also studied. Experimental data, when fitted on various kinetic data showed the first order kinetic model to be most suited, while others viz. zero, second, parabolic diffusion and elovich equations were rejected.

Key words: Leaching, Kinetics, Soil, Kota, Adsorption, Desorption.

INTRODUCTION

The various processes like low leaching of the salts, evaporation of soil water and different human activities[1] contribute to the salt accumulation in soil. The accumulated soluble salts are mainly chlorides and sulphates of Na, Ca and Mg. With increase in concentration of soil solution, the Ca and Mg salts are precipitated[2], resulting in the increased relative proportion of Na. Thus, Na becomes the dominant exchangeable cation in the salt solution and plays a major role in the salinization of soil. On account of high solubility of its compounds, the excessive Na easily gets leached through the soil which at the one end contaminates the ground water[3,4] and excessive Na on the exchange complex site enhances the swelling[5-7] and the dispersion[8] of soil colloids on the other. Dikinya et al.[9] reported the decrease of permeability to mobilization and re-deposition of fine particles, using a monovalent NaCl electrolyte solution. Problems related to the use of sodic/saline waters are global[10] especially in arid and semi-arid soils, where the sodium and calcium ions

*Author for correspondence; E-mail: ashu.uok@gmail.com

are the most common ions on the exchange complex. Ion exchange reactions of Na^+ and Ca^{2+} and available Na/Ca ratio of the soil are the important factors which affect the leaching of Na^+ to the great extent. Many previous studies carried out by Qadir et al.[11] and Ghafur et al.[12] revealed that Na-Ca exchange reactions also form the basis of reclamation of saline-sodic soils[13]. However, there is a little research data available with regard to leaching of sodium in heterogeneous soil system and therefore, the present work was aimed at studying the effect of various factors, such as varying temperature, varying concentration of added Na in soil system and on the leaching of sodium under simple laboratory conditions. The Na-Ca exchange behavior was also studied by introducing the varying concentration of Ca in percolating water.

EXPERIMENTAL

Materials and methods

The clay loam soil collected from Kota was sun dried and sieved for uniform particle size (300 µm). Columns of 60 x 3 cm^2 were prepared surrounded by glass jacket of continuously flowing thermostated water. 60 g soil was filled in the column and was gently packed at water filled porosity of 0.11 cm^3 cm^{-3}. The flow rate of the extractant was maintained constant (2 ± 1 mL min^{-1}). A fixed volume of aqueous salt solution with desired cation concentration was added on the top of the soil column in each experiment. The salt solution was allowed to get adsorbed uniformly for 24 hours, after which continuously leached with de-ionized water or with other extractants as per requirement of the study. The leaching was carried out till the soluble cations were completely removed from the column soil. For calculating initial leaching rates, the concentration of sodium was determined in leachates collected in batches at the interval of 5 minutes, using Flame photometer (Systronics Model 128). The total leached concentration was taken equal to the total leachable content present at t = 0. The concentration terms determined in mg/L were converted into mg/kg in soil during kinetic calculations. The treatment of results obtained in leaching study of Na is based on the calculations of initial leaching rates as well as on application of various kinetic models. The concentration terms used for presenting the analytical results are –

$[Na^+]_s$ = Leachable Na present in column soil, 100 mg/kg

$[Na^+]_{ad}$ = Na concentration introduced or added in the soil column

$[Na^+]_i$ = Total leachable concentration present initially in mg/kg

$[Na^+]_{fixed}$ = Na entrapped in soil micelle i.e. Na^+ concentration retained in the column.

$[Na^+]_{extra}$ = Concentration of unleachable sodium converting into leachable sodium.

$[Na^+]_t$ = Leached concentration at time 't'

$[Na^+]_i$ = $[Na^+]_i - [Na^+]_t$ = Leachable concentration remaining at time 't'

RESULTS AND DISCUSSION

The experimental soil inherently possesses 100 mg/kg of leachable sodium. On adding varying concentrations of NaCl in experimental soil column, Na leaching is witnessed incorporating $[Na^+]_{fixed}$ and $[Na^+]_{extra}$ along with $[Na^+]_i$. The values of $[Na^+]_i$, $[Na^+]_{fixed}$, $[Na^+]_{ex}$ at various $[Na^+]_{ad}$ are given in Table 1.

Table 1: The values of $[Na^+]_i$, $[Na^+]_{fixed}$ and $[Na^+]_{extra}$ at different $[Na^+]_{ad}$ for NaCl at 30^0C; soil = 60 g; θ = 0.11 cm^3cm^{-3}

$[Na^+]_{ad}$ mg/kg	$[Na^+]_i$ mg/kg	$[Na^+]_{fixed}$ mg/kg	$[Na^+]_{extra}$ mg/kg
0	100	-	-
65.52	110	55.52	-
262.1	380	-	17.9
524.2	682	-	57.8
786.32	942	-	55.7

It is observed that Na was adsorbed at lower $[Na^+]_{ad}$ values only while at higher $[Na^+]_{ad}$ concentration i.e. 262 mg/kg and above, $[Na^+]_{ex}$ was observed which can be attributed to the negative adsorption phenomenon introduced by Matson[14] explaining that any ion on any clay or soil can be distributed unequally in the diffuse double layers of soil, which may come out of the soil during leaching. Previously the phenomenon of negative adsorption was observed in Cl^- leaching[14]. At very high NaCl added conditions, the unleachable sodium inherently present in the column soil converts into leachable one due to Ca-Na and Na-K exchange as the affinity of Ca and K to bind at cation-exchange sites of soil particles is higher than the Na.

Leaching rate profiles

Initial rate of leaching, LR_{obs} represents the rate of change in leachable concentrations of $[Na^+]_i$ with time. LR_{obs} values are obtained from the initial slopes of the plots between $[Na^+]_i$ vs. time as shown in Fig. 1.

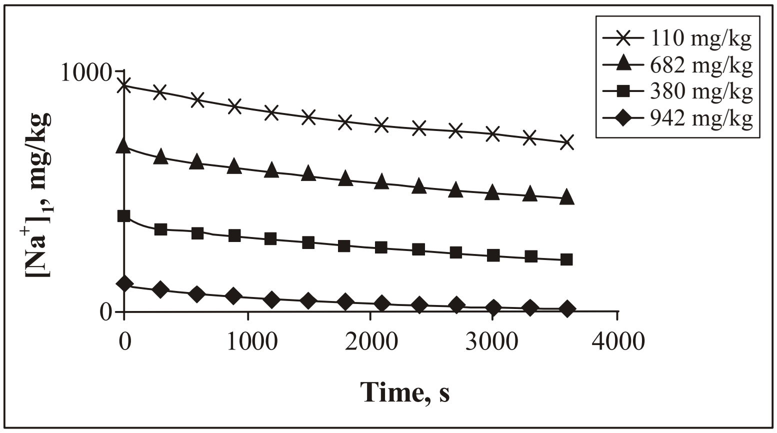

Fig 1: Initial leaching rate profiles for NaCl at different $[Na^+]_i$ concentrations at 30^0C ; Soil = 60 g ;θ = 0.11 cm^3cm^{-3}

It can be seen clearly from the Fig. 1 that leaching of $[Na^+]_i$ increases linearly on increasing concentration of added salt in the soil column. This is due to increase in leached sodium concentration, $[Na^+]_i$, at higher $[Na^+]_{ad}$. The dependence of LR_{obs} on $[Na^+]_i$, for NaCl leaching is shown in Fig. 2.

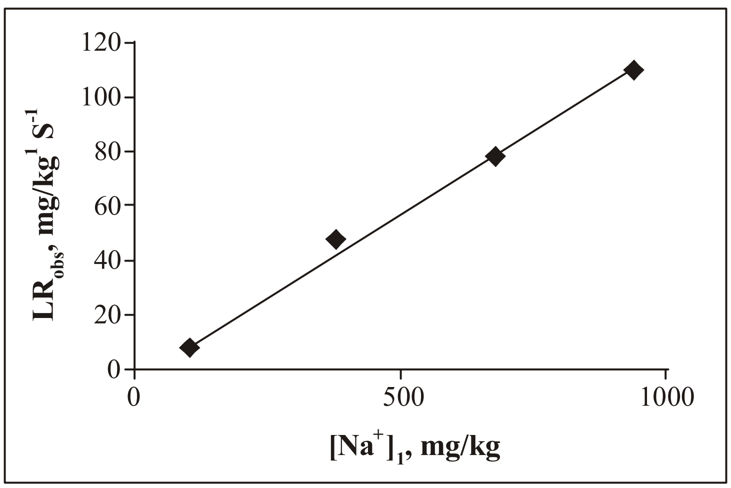

Fig. 2: Variation in LR_{obs} at different $[Na^+]_i$ concentrations for NaCl leaching at 30^oC ; Soil = 60 g ; θ = 0.11 cm^3cm^{-3}.

The Na leaching rates are found to fit into following rate law equation (1).

$$LR_{obs} = k\,[Na^+]_i^{n} \qquad \ldots(1)$$

From the log-log plots of $[Na^+]_i$ vs. LR_{obs}, values of k and n are calculated as 2.08 x 10^{-2} sec^{-1} and 1.2, respectively (Coefficient of determination r^2 = 0.985, standard error of estimate = 0.077).

Effect of temperature

The effect of temperature on $[Na^+]_i$ and LR_{obs} was studied in the range of 20°C – 50°C. $[Na^+]_i$ as well as LR_{obs} were found to increase with rise in temperature for a fixed $[Na^+]_{ad}$ of 150 mg/kg (Table 2).

Table 2: Effect of temperature on $[Na^+]_i$ and LR_{obs} values for leaching of NaCl at $[Na^+]_{ad}$ = 150 mg/kg . Soil = 60 g ; θ = 0.11 cm^3cm^{-3}.

Salt	Blank		NaCl	
Temp. °C	$[Na^+]_i$, mg/kg	LR_{obs} mg/kg^{-1}s^{-1}	$[Na^+]_i$, mg/kg	LR_{obs}, mg/kg^{-1}s^{-1}
20	96	7.68	153	14.2
30	100	7.8	160	14.4
40	109	7.9	172	14.6
50	115	8.1	162	14.4

From the results, it is clear that with increasing temperature, the solubility of different sodium salts increases and the adsorption on soil decreases, resulting in the higher LR_{obs} and $[Na^+]_i$ values. Increase in rate of solubility of salts prevents the adsorption of ions on to the soil reactive sites[15]. Salts having increase in solubility with increase in temperature will leach more at higher temperatures[16].

Effect of Ca^{2+} level of extractant

Calcium levels of extractant water was varied from 100 ppm to 500 ppm by addition of Ca^{2+} in the form of $CaCO_3$. Hardness effect on leaching was studied on soil column on a fixed $[Na^+]_{ad}$ concentration of 261 mg/kg.

There is a decrease in $[Na^+]_i$ and LR_{obs} with increase in $CaCO_3$ content of percolating water (Table 3).

This may be due to Na-Ca exchange, which changes the amount of exchangeable Na in soil matrix; thus amount of $[Na^+]_{fixed}$ increases and leachable quantity of Na is decreased. Dikinya and Totolo[17] applied the Gapon's equation on Na-Ca exchange and observed that on decreasing the ratio of Na/Ca in soil, the amount of exchangeable Na decreases while exchangeable Ca increases. Our results were found similar with some previous studies[19,20] which also reported decrease in $[Na^+]_i$ and increase in $[Na^+]_{fix}$ with increasing level of Ca^{2+} or on lowering of Na/Ca ratio (Table 3).

Table 3: The values of $[Na^+]_i$, $[Na^+]_{fixed}$ and $[Na^+]_{extra}$ at different $[Ca^{2+}]_{ad}$ for NaCl at a fix $[Na^+]_{ad}$ = 261 mg/kg at 30^{0}C; Soil = 60 g; θ = 0.11 cm^3cm^{-3}.

$[Ca^{2+}]_{ad}$ mg/kg	$[Na^+]_i$ mg/kg	$[Na^+]_{fixed}$ mg/kg	$[Na^+]_{extra}$ mg/kg
0	380	-	19
100	300	61	-
200	270	91	-
500	200	161	-

Plot constructed for $[Ca^{2+}]_{ad}$ vs. LR_{obs} (Fig. 3) also support our view.

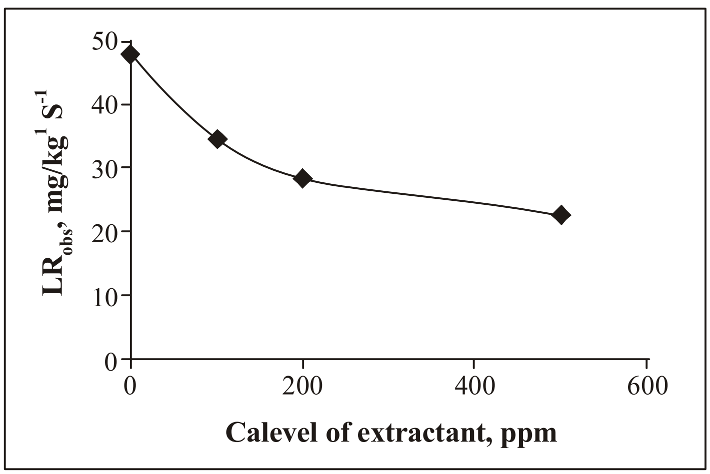

Fig. 3: Effect of Ca level of extractant on LR_{obs} at a fix $[Na^+]_{ad}$ = 261 mg/kg at 30^{o}C

Application to the kinetic models

The data for the leaching of sodium salts in alkaline soils were applied on zero order, first order, second order, Elovich equation and parabolic diffusion kinetic models. All the models were tested with least square regression analysis. The zero order kinetic model plots were found to be similar to the initial rate plots (Fig. 1). First order kinetic model plots are shown in Fig. 4.

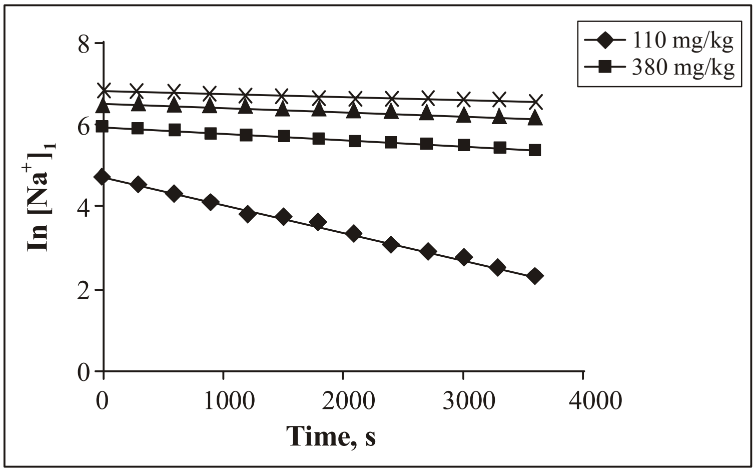

Fig 4: First order equation profile for NaCl leaching at different $[Na^+]_i$ at 30° C.

The values of statistical parameters are given in Table 4. Out of various kinetic models for representing Na^+ leaching, first order kinetic model is found to be the best suited one, showing higher values of r^2 and lowest SEE values, whereas other kinetic models were rejected, which proves that concentration of soluble salts is most important for determining the rate of leaching in subsurface water.

Table 4: Coefficient of determination (r^2), standard error of estimate (SEE) and slope for graphical equations of different kinetic models applied on $[Na^+]$ leaching at different $[Na^+]_i$ for NaCl at 30° C . Soil = 60 g ; θ = 0.11 cm^3cm^{-3}.

$[Na^+]_{ad}$	110			380			682			942		
Para-meters	r^2	slope	SEE	r^2	slope	SEE	r^2	slope	SEE	r^2	slope	SEE
Zero order	0.895	-0.02	10.81	0.961	-0.04	10.27	0.976	-0.05	10.77	0.960	-0.06	15.55
First order	0.994	-0.00	0.058	0.984	-0.00	0.0231	0.988	-0.00	0.0133	0.974	-8×10^{-5}	0.0154
Second order	0.902	2×10^{-5}	0.009	0.993	5×10^{-7}	5.2×10^{-5}	0.995	2×10^{-7}	1.5×10^{-5}	0.984	10^{-7}	1.4×10^{-5}
Elovich	0.987	34.08	3.02	0.938	53.08	10.92	0.939	73.73	14.88	0.974	84.73	10.967
Parabolic	0.969	1.887	4.725	0.990	3.088	4.36	0.992	4.236	5.14	0.996	4.788	4.15

Since less work has been performed on leaching of Na^+ in soil system and soil used in present work may have different physico-chemical properties, an appropriate comparison of our study with previous studies cannot be made.

CONCLUSION

The evaluation presented in the present paper concludes that addition of Ca in irrigation water controls excessive leaching of Na; thus, gives a solution to the problems of sodic- saline soils. The increased temperature of the soil promotes the leaching of salt by increasing its solubility.

Phenomena of negative adsorption observed in case of higher sodium concentrations concludes that soil has no absorbing capacity for the added Na. It is not at all adsorbed in the soil rather fixed in the matrix. Naturally present Na in the soil is also desorbed due to its high affinity to the chloride ions than any other inorganic anion or organics of the soil.

The present results are important to deliberate on the leaching of sodium enriched alkaline soil at higher level of chloride ions at different temperatures and hardness of percolating water.

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