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THE LEACHING KINETICS AND THERMODYNAMICS STUDIES OF CHLORIDE [CL] IN ALKALINE SOIL OF KOTA REGION AROUND CHAMBAL COMMAND AREA [CCA] THROUGH VERTICAL FLOW USING GLASS COLUMN METHOD UNDER THE INFLUENCE OF ADSORPTION AND DESORPTION PROCESS MADE BY ADDING MONOVALENT, BIVALENT AND TRIVALENT EFFLUENTS.

Chemistry

Neelam Chaudhary* Research Scholar Department Of Chemistry Career Point University, India. *Corresponding Author

Dr. Bharatiy Sharma Associate Professor And Head M.B.P.G. College, Kota.

ABSTRACT

Leaching kinetics and thermodynamics of chloride by loading various effluents on undisturbed vertical soil columns has been studied and relation between leachable chloride concentration $[Cl^-]_L$ and rate of leaching $[L_R]$ has been investigated within a time interval $[t_L]$ by increasing temperature. The advanced research work is focused on downward transportation of chloride influenced by adding variable concentration of monovalent, bivalent and trivalent effluents $[Cl^-]_{eff}$ within a time interval with changing temperature $[T_L]$ occurring the range of 20ºC to 40ºC in Rajasthan climate annually. Total leachable concentration of chloride $[Cl^-]_{TL}$ was found unaffected by incubation time $[t]_{inc}$ while first order model is found to be fit for representing chloride leaching in the entire conditions of the lab experiments. The entire research work has been completed by graphical representation, mathematical modeling, statistical interpretation of collected data from leaching kinetics and thermodynamics studies of chloride in alkaline soil of Kota region through vertical flow using glass column method under the influence of adsorption and desorption process made by adding effluents.

KEYWORDS

Leaching, Effluents, Kinetics, Thermodynamics, Downward Transportation, Incubation Time.

To achieve food securing in thecountry the efforts have to make on area expansion under agriculture by restoring the degraded lands as well as rise in crop productivity besides crop storages for a long. Nearly 147 million ha of land is subjected to soil degradation, including 94 million ha from water erosion, 23 million ha from salinity 14 million ha from water logging, 9 million from wind erosion and 7 million ha from a combination of factors due to different forces in India. In this way in a considerable wide area of India has the development of the twin problem of waterlogging and soil salinization resulted going out of production or experiencing reduced yield with the introduction of irrigated agriculture in arid and semi arid region. (Bhattacharya, 2015)[1] . Annual variability in rainfall pattern (Shekhar et al, 2011)[2] , high evaporation (Roader et al, 1998)[3] , lead salt accumulation. Salinity stress in arid and semi arid effects and manage the field crops (Sajid Husain et al, 2019)[4] . The ICAR (Central Soil Salinity Research Institute) and many state universities suggest, that every year nearly 10% additional area is getting salinize and by 2050, around 50% of the fertile land would be salt affected and developing reclamation technologies and strategies (Foster. S et al, 2018)[5] In order to sort out the problem of water logging and soil salinity a lots of efforts are invented to achieve like drainage research (IDNP, 2002)[6] gypsum based sodic soil reclamation developing salt tolerance crop varieties [Mokhtar et al, 2019][7] improving agro forestry technologies in the country [Pradeep and Pradeep, 2020][8] . A lots of research work has admitted glass column method's accuracy for study of leaching various nutrients or ions within controlled condition in the lab dispite of different climates in world (Singh et al, 2012[9] ; chezom et al, 2013[10] ; ASTM P. 4-78, 74-95, 2014[11] ; S.B. Patil and H.S. Chore, 2015)[12] . Durin the research work leaching of chloride concentration changes were noticed with adding effluents monovalent, bivalent, trivalent effluents containing chloride anion [S.K.Sharma, 1996[13] ; Mamoun et al, 2009][14] . It was observed during the leaching of chloride from the soil that the total leachable chloride concentration $[Cl^-]_{TL}$was not equal to leachable chloride concentration $[Cl^-]_L$ because of formation of chloride in the complex form $[Cl^-]_{comx.}$ but as valency increase with NaCl, $CaCl_2$, $AlCl_3$ compounds adding leachable chloride concentration $[Cl^-]_L$ and Chloride in the complex form $[Cl^-]_{comx.}$ both increase however only leachable chloride concentration $[Cl^-]_L$ was measurable through Argentometric titration method and changes can be seen in leachable chloride concentration $[Cl^-]_L$ in different conditions. Although leaching of nutrients and ion has been studied through soil profile but very less work has been done to see the kinetics and thermodynamics changes during leaching. [Rath P.C. et al, 1988[15]; A.C. Garrabrants et al, 2012[16]; S.Heuss and O. Sagar, 2013[17]; Sharma et al, 2018][18]

Area selected for study –

Zone A : Anta	Zone B : Ladpura	Zone C : Sultanpur
Sub urban & Industrial Area having good plantation	Urban area, high traffic pollution with industrial area.	Sub urban & rural area having good plantation

MATERIAL - METHOD - Procedure -

The estimation of Cl^- were done in Mg/L from study area zone A, Zone B and Zone C in different seasons varied from 85 to 365 but finally the sample were taken for kinetic and thermodynamic studies with chloride concentration $[Cl^-]_i$ of 100 Mg/L for zone A, 120 Mg/L for Zone B, 111 Mg/L for zone C. The soil samples were collected, dried and sieved for uniform particle size (300 µm) from study area zone A, zone B and zone C around Kota city.Length of 60 cm and diameter of 3 cm^2 glass columns were prepared 60 gm soil was gently packed at water filled porosity of 0.11 $cm^3\ cm^{-3}$ and filled in the column. A fixed volume of desired aqueous salt like NaCl, $CaCl_2$, $AlCl_3$ with a particular concentration was added from the top of the soil columns were allowed to get absorbed uniformly in the column for 24 hours in each experiment to maintain constant flowrate 20 ml/10 minute the column were leached with deionized water tillcomplete leaching of chloride ions. leachable concentration of chloride $[Cl^-]_L$ was measured at fixed time while unleachable compound of chlorides, which may exist as in Chloride Complexed form $[Cl^-]_{compx.}$ was measured after experiment by adding the column soil into known volume of extractants.

$$(Cl^-)_{eff})NaCl = (Cl^-)_{eff})_{xCl_2} = (Cl^-)_{eff})_{xCl_3} = 20mg/l$$

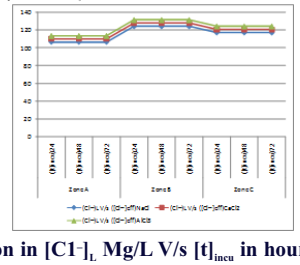

Fig. 1 : Variation in $[C1^-]_L$ Mg/L V/s $[t]_{incu}$ in hours with different addition of $[C1^-]_{eff}$ in Zone A, Zone B and Zone C at room temperature.

As total leached concentration of chloride $[Cl^-]_L$was taken equal to the total leachable chloride concentration $[Cl^-]_{TL}$ i.e

$$(Cl^-)_1 + (Cl^-)_2 + \ldots + (Cl^-)_n = [Cl^-]_n$$

present at t = 0 where n = number of leached chloride concentration [Cl–]L after each experiment till the complete leaching of chloride through the soil in the glass column where $(Cl^-)_1$ refers to first time noticed leaching of chloride concentration $[Cl^-]_L$ and $(Cl^-)_n$ refers to last leached chloride concentration noticed during each experiment. Chloride concentration in Mg/L was measured by simple titration

method using $AgNO_3$, keeping column length flow rate, pH of percolating water and temperature, constant during all the kinetics except during temperature variation studies.

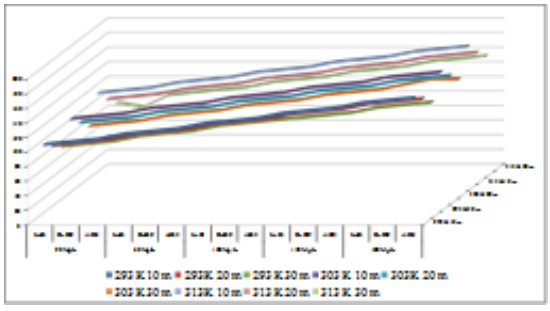

Figure : 2; Leaching Rate Profile Zone -A; $([Cl]_L)_n$ in Mg/L V/s $([Cl]_{eff})_{NaCl}$ in [3.4, 10.3, 17.1, 23.9, 30.8] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/L respectively, $([Cl]_{eff})_{CaCl_2}$ in [1.8, 5.4, 9.0, 12.6, 16.2] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/ L respectively, $([Cl]_{eff})_{AlCl_3}$ in [1.5, 4.5, 7.5, 10.5, 13.5] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/L respectively, V/s $[t_L]_0$, $[t_L]_{10}$, $[t_L]_{20}$ in min, V/s $[T_L]_{293K}$, $[T_L]_{303K}$, $[T_L]_{313K}$ in Kelvin

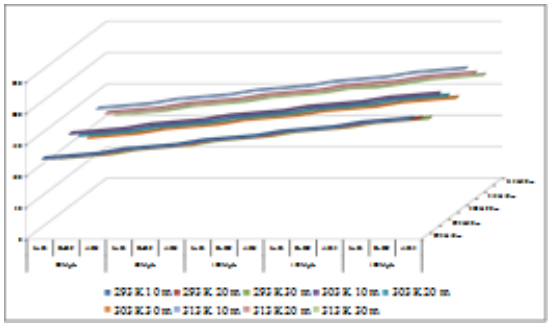

Figure : 3; Leaching Rate Profile Zone - B; $([Cl]_L)_n$ in Mg/L V/s $([Cl]_{eff})_{NaCl}$ in [3.4, 10.3, 17.1, 23.9, 30.8] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/L respectively, $([Cl]_{eff})_{CaCl_2}$ in [1.8, 5.4, 9.0, 12.6, 16.2] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/ L respectively, $([Cl]_{eff})_{AlCl_3}$ in [1.5, 4.5, 7.5, 10.5, 13.5] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/L respectively, V/s $[t_L]_0$, $[t_L]_{10}$, $[t_L]_{20}$ in min, V/s $[T_L]_{293K}$, $[T_L]_{303K}$, $[T_L]_{313K}$ in Kelvin

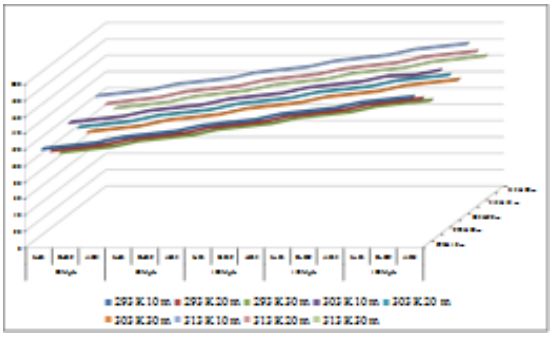

Figure : 4; Leaching Rate Profile Zone - C; $([Cl]_L)_n$ in Mg/L V/s $([Cl]_{eff})_{NaCl}$ in [3.4, 10.3, 17.1, 23.9, 30.8] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/L respectively, $([Cl]_{eff})_{CaCl_2}$ in [1.8, 5.4, 9.0, 12.6, 16.2] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/ L respectively, $([Cl]_{eff})_{AlCl_3}$ in [1.5, 4.5, 7.5, 10.5, 13.5] $\times 10^{-4}$ M or [2, 6, 10, 14, 18] $\times 10$ Mg/L respectively, V/s $[t_L]_0$, $[t_L]_{10}$, $[t_L]_{20}$ in min, V/s $[T_L]_{293K}$, $[T_L]_{303K}$, $[T_L]_{313K}$ in Kelvin

RESULT AND DISCUSSION

Variation of incubation period :

It's clear from leaching rate profile as incubation time $[t]_{incu}$ variations or variation in incubation period was done on 24 hours, 48 hours, 72 hours at the fixed concentration of effluents i.e.

$$(Cl^-)_{eff} = \left([Cl^-]_{eff}\right)_{NaCl} = \left([Cl^-]_{eff}\right)_{CaCl_2} = \left([Cl^-]_{eff}\right)_{AlCl_3} = 20\text{Mg / L}$$

leaching concentration of chloride at a fix time $[Cl^-]_L$ and observed leaching rate $[L_R]$ were too stable.

Chloride Leaching Kinetics :

As ions concentration $[Cl^-]_L$ were measured continuously in leached solution till complete removing of soluble ions in the column soil with adding effluents as per requirement of the study, or graph plotting of $[Cl^-]_L$ with time interval taken for leaching $\Delta[t_L]$ give leaching rate profiles the chloride 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 $[Cl^-]_{TL}$ was taken equal to the total leachable concentration present at $[t_L] = 0$ as

$$\left[Cl^-\right]_{TL} = \left([Cl^-]_L\right)_{n_1} + \left([Cl^-]_L\right)_{n_2} + \ldots \left([Cl^-]_L\right)_{n_i}$$

Chlorides leaching thermodynamics

Leaching rate profile predict clearly changes in chloride leaching concentration $[Cl^-]_L$ with temperature $[T_L]_{293K}$, $[T_L]_{303K}$ and $[T_L]_{313K}$. With increasing temperature slightly increasing behavior in leaching rate of chlorides is observed. A high value of activation energy reported to true ion exchange during leaching. Noticeable changes were seen in graph plotting lnk in min^{-1} V/s $\frac{1}{[T_L]}$ in K–1.

CONCLUSION

This study was conducted to find out Chloride leaching concentration $[Cl^-]_L$ variabilities with addition of different effluent $[Cl^-]_{eff}$ with different concentration in a particular Temperature range $\Delta[T_L]$ which occur annually in Rajasthan. All plotted graph and predict in easy way these all kind of changes. This study have a multidisciplinary approach to obtain leaching kinetics and thermodynamics data and these better representation through tables and graphs.

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