



**ORIGINAL RESEARCH PAPER**

**Mathematics**

**MATHEMATICAL KINETIC AND THERMODYNAMIC STUDY OF ADSORPTION OF COMPETITOR ION AS CHLORIDE I, FLUORIDE I AND NITRATE I ON ALKALINE SOIL USING BATCH METHOD**

**KEY WORDS:** Equilibrium constant, Kinetic parameter, Enthalpy changes, Free energy changes, Entropy changes, CCA

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**ABSTRACT**

The CCA Rajasthan is career out to constraint their solute sources and subsurface weathering process sodium, chloride, fluoride, calcium ions dominate major ion chemistry. This type of chemistry have been pointed to a significant solute supply from the salt affected soils and bedrock dissolution. Annual changes model calculations involving elemental ratios of major ions show that the solutes are mainly supplied through salt affected soils with climatic or manual inputs. These estimates are consistent with abundant ions like chloride, fluoride and nitrate ions regards leaching kinetics and thermodynamics parameters comparatively. The faster or slower kinetics or thermodynamics were observed clearly during annual research. The out comes of this study underscore distinctly different leaching rate profiles following first order reaction mainly with entropy and enthalpy variabilities in the reference of the particulars ions in alkaline soils using batch process method. These entire study when is modified or made graphically represented by statistical parameters through mathematical modelling make the way to sustain the profitable changes for escaping soil salinity or ground water or surface water and soil qualities protections, so in this way main purpose of this work is to comparatively study the adsorption of calcium, magnesium and sodium as  $-Cl, -F, -NO$  ions on to the soil sample (SS) suffered from salinity around the Chambal Command Area (CCA) to get the equilibrium constant, enthalpy changes, Gibbs free energy changes, entropy changes respectively  $[k_{eq}], [\Delta H^0], [\Delta G^0], [\Delta S^0]$ . The series of experiments were done with different amount and concentrations of adsorbate or effluents as  $([Cl]_{eff})_{CaCl_2}, ([F]_{eff})_{CaF_2}, ([NO_3]_{eff})_{CaNO_3}$  in the temperature range of 293K to 313K by using batch process method. Although rates of adsorption [AdR] or rates of unadsorption [UadR] were found almost 1st order during entire experiment but to get the clear prediction, distributions, classifications, assumptions and make ease to understand mathematical modeling was done with the help of statistical parameters in order to find the ways to escape soil salinity drawbacks scientifically.

**Introduction**

The ground water is the predominant water resource for domestic and agricultural needs, particularly in arid and semiarid regions with limited surface water availability.<sup>(1,2)</sup> In these regions, the ground water recharge rate is lower than its withdrawal rate.<sup>(2,3)</sup> A gradual deteriorating quality of surface water, ground water and soil salinity caused by many anthropogenic factors, climatic changes, soil weathering or precipitation + evaporation, accumulated salt or related ions exchange capacities competition at experimental level<sup>(3,4)</sup> furthermore, the climatic change scenario and unpredictable intensity and frequency of precipitation + evaporation led to change in leaching kinetics and thermodynamics annually in saline soil.<sup>(4,5)</sup> Although canal area become more suffered from soil salinity because of water

logging is mainly subjected to ions like  $Cl, F, NO_3$  exchange capacities abundant in the particular area so having higher specific gravity  $CaCl_2, CaF_2$  and

$CaNO_3$  salts were selected by adding different concentration with different amount of effluents as  $([Cl]_{eff})_{CaCl_2}, ([F]_{eff})_{CaF_2},$

$([NO_3]_{eff})_{CaNO_3}$  containing salts during a range of temperature  $[T]_{293K}, [T]_{313K}$  resulting a variety of leaching rate profile  $[L_R]$  were obtained in

order to get the kinetics and thermodynamics parameters.<sup>(5,6)</sup> The reactions order was found 1<sup>st</sup> order during each experiment. Adsorption efficiency of ions describes residential or uptake time of the adsorbate on adsorbant at the solid solution interface.<sup>(7,8)</sup> Directional or non directional operations of the ions adsorption and remedial operations scaling up studies of soil remediation processes connecting ambient factors give the kinetic and thermodynamic results during duo opposite factors of adsorption-desorption process frequently.<sup>(9)</sup> Using by batch process method various parameters studied in a range of temperature  $[T]_{293K}, [T]_{313K}$  by adding

various amount of salt. In order to understand adsorption efficiency of ions adsorption kinetic studies were done which describe residential or uptake time of solute on solvent at the solid solution interface<sup>(10)</sup>. The kinetical parameters can scale up studies of soil remediation process connecting optimum operational conditions of competitor ions predicting by important directional or non-directional operations of the ion adsorption and remedial operations.<sup>(11)</sup> As temperature can make two types effects on the adsorption process as physical adsorption and chemical adsorption process which are opposite qualities in the reference of increasing temperature.

So only temperature changes are not sufficient parameter to determine the type of adsorption.<sup>(6)</sup> Thus enthalpy change  $[\Delta H^0]$  Gibbs free energy change  $[\Delta G^0]$  and entropy change  $[\Delta S^0]$  were too observed and calculated of each experiment to know whether the reactions are spontaneous or non spontaneous or feasible.

$[\Delta G^0]$  was found negative<sup>(8)</sup> while  $[\Delta H^0]$  was distinct positive<sup>(12)</sup> and finally mathematical modeling were done of entire data to make ease to understand with the adsorption-desorption of mutually competitor ions with the help of statistical parameters.

**Material and Methods :**

For the estimation of  $Cl, F, NO_3$  amount or concentration during adsorption or desorption process on the soil sample [SS], the soil sample were collected, dried and sieved for removing unwanted particles, from study region. Length 60cm and diameter of 3cm of glass column was prepared and gently packed or filled with 60gm soil. A fixed amount of salt as effluent as  $([Cl]_{eff})_{CaCl_2}, ([F]_{eff})_{CaF_2}, ([NO_3]_{eff})_{CaNO_3}$  were added in the temperature range of  $[T]_{293K}$  to  $[T]_{313K}$  according to Rajasthan climate. In thermostat conditional concentration change of  $Cl, F, NO_3$  were noticed

and with the help of adsorbed amount of ions  $[AC]_{ad}$  and unadsorbed amount of ions  $[AC]_{uad}$ , equilibrium constant  $k_{eq} = \frac{k_{ad}}{k_{uad}} = \frac{[AC]_{uad}}{[AC]_{ad}}$  were

noticed for further kinetics and thermodynamics studies enthalpy  $[\Delta H^\circ]$  by van't hoff equation  $\frac{d \ln k}{dT} = \frac{\Delta H^\circ}{RT^2}$  or  $\ln\left(\frac{k_2}{k_1}\right) = \frac{\Delta H^\circ}{8.314} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$

Gibbs energy by the following equations  $\Delta G^\circ = -RT \ln k_e$ ,  $\Delta S^\circ$  by the following equation  $\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$  were calculated consequently in

order to know reaction feasibility or spontaneity. The treatment of calculation of obtained data is based on the some parameter as defined below.

$[SS]$  – Soil sample

$[AC]_{ad}$  – Concentration of ions as  $Cl^-$ ,  $F^-$ ,  $NO_3^-$  adsorbed on adsorbent in mg.

$[AC]_{uad}$  – Concentration of ions as  $Cl^-$ ,  $F^-$ ,  $NO_3^-$  unadsorbed on adsorbent in mg

$[k_{eq}]_{293K}^{Chl}$  – Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 293K regards  $Cl^-$

$[k_{eq}]_{313K}^{Chl}$  – Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 313K regards  $Cl^-$

$[k_{eq}]_{293K}^{Fl}$  – Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 293K regards  $F^-$

$[k_{eq}]_{313K}^{Fl}$  – Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 313K regards  $F^-$

$[k_{eq}]_{293K}^{Nit}$  – Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 293K regards  $NO_3^-$

$[k_{eq}]_{313K}^{Nit}$  – Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 313K regards  $NO_3^-$

$[T]_{293K}$  – Temperature of 293 K maintained during experimental work in kelvin.

$[T]_{313K}$  – Temperature of 313 K maintained during experimental work in kelvin.

$\left([Cl]_{eff}\right)_{CaCl_2}$  –  $Cl^-$  salt added from the top of glass column as effluent or adsorbate mg/gm

$\left([F^-]_{eff}\right)_{CaF_2}$  –  $F^-$  salt added from the top of glass column as effluent or adsorbate mg/gm

$\left([NO_3^-]_{eff}\right)_{CaNO_3}$  –  $NO_3^-$  salt added from the top of glass column as effluent or adsorbate mg/gm

$[\Delta H^\circ]_{293K-313K}^{Chl}$  – Linthalpy change with the temperature, reference of  $Cl^-$  change in kilo joule per mole  $KJmol^{-1}$

$[\Delta H^\circ]_{293K-313K}^{Fl}$  – Fenthalpy change with the temperature, reference of  $F^-$  change in kilo joule per mole  $KJmol^{-1}$

$[\Delta H^\circ]_{293K-313K}^{Nit}$  – Fenthalpy change with the temperature, reference of  $NO_3^-$  change in kilo joule per mole  $KJmol^{-1}$

$[\Delta G^\circ]_{293K-313K}^{Chl}$  – Gibbs free energy change with the temperature, reference of  $Cl^-$  change in kilo joule per mole  $KJmol^{-1}$

$[\Delta G^\circ]_{293K-313K}^{Fl}$  – Gibbs free energy change with the temperature, reference of  $F^-$  change in kilo joule per mole  $KJmol^{-1}$

- $[\Delta G^\circ]_{293K-313K}^{Nit}$  – Gibbs free energy change with the temperature, reference of  $NO_3$  change in kilo joule per mole  $KJmol^{-1}$
- $[\Delta S^\circ]_{293K}^{Chl}$  – Entropy change with the 293 K temperature, reference of  $Cl^-$  change in joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{293K}^{Fl}$  – Entropy change with the 293 K temperature, reference of  $F^-$  change in joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{293K}^{Nit}$  – Entropy change with the 293 K temperature, reference of  $NO_3$  change in joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{313K}^{Chl}$  – Entropy change with the 313 K temperature, reference of  $Cl^-$  change in Joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{313K}^{Fl}$  – Entropy change with the 313 K temperature, reference of  $F^-$  change in Joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{313K}^{Nit}$  – Entropy change with the 313 K temperature, reference of  $NO_3$  change in Joule per kelvin per mole  $JK^{-1}mol^{-1}$

**Table 1 :** Determination of kinetic and thermodynamic parameters  $[k_{eq}]_{293K}^{Chl}$ ,  $[k_{eq}]_{313K}^{Chl}$ ,  $[\Delta H^\circ]_{293K-313K}^{Chl}$ ,  $[\Delta G^\circ]_{293K-313K}^{Chl}$ ,  $[\Delta S^\circ]_{293K}^{Chl}$ ,  $[\Delta S^\circ]_{313K}^{Chl}$  with the addition of various amount of salt  $([Cl^-]_{eff})_{CaCl_2}$  as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$  and  $[T]_{313K}$ .

$([Cl^-]_{eff})_{CaCl_2}$	$[k_{eq}]_{293K}^{Chl}$	$[k_{eq}]_{313K}^{Chl}$	$[\Delta H^\circ]_{293K-313K}^{Chl}$	$[\Delta G^\circ]_{293K-313K}^{Chl}$	$[\Delta S^\circ]_{293K}^{Chl}$	$[\Delta S^\circ]_{313K}^{Chl}$
25	3.18	3.83	7.67	-5.09	16.53	16.50
50	3.00	3.27	7.62	-1.60	49.91	49.96
75	2.78	3.07	7.56	-0.28	36.06	36.02
100	2.26	2.71	7.87	-1.62	34.83	34.71
125	1.17	2.18	7.93	-0.67	31.80	31.73
150	1.01	1.52	8.12	-0.13	34.02	34.01
175	0.48	1.06	8.15	-0.00	34.63	34.62
200	0.27	0.88	8.39	-0.93	34.21	34.16
225	-0.01	0.23	8.48	-0.82	33.02	32.02

**Table 2 :** Determination of kinetic and thermodynamic parameters  $[k_{eq}]_{293K}^{Fl}$ ,  $[k_{eq}]_{313K}^{Fl}$ ,  $[\Delta H^\circ]_{293K-313K}^{Fl}$ ,  $[\Delta G^\circ]_{293K-313K}^{Fl}$ ,  $[\Delta S^\circ]_{293K}^{Fl}$ ,  $[\Delta S^\circ]_{313K}^{Fl}$  with the addition of various amount of  $([F^-]_{eff})_{CaF_2}$  as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$  and  $[T]_{313K}$ .

$([F^-]_{eff})_{CaF_2}$	$[k_{eq}]_{293K}^{Fl}$	$[k_{eq}]_{313K}^{Fl}$	$[\Delta H^\circ]_{293K-313K}^{Fl}$	$[\Delta G^\circ]_{293K-313K}^{Fl}$	$[\Delta S^\circ]_{293K}^{Fl}$	$[\Delta S^\circ]_{313K}^{Fl}$
25	3.11	3.81	7.66	-6.29	15.52	15.48
50	2.92	3.25	7.63	-5.46	47.93	47.76
75	2.70	3.01	7.97	-1.41	35.01	34.86
100	2.21	2.92	7.86	-0.81	33.83	33.70
125	1.10	2.52	7.92	-0.93	30.80	30.72
150	0.93	1.48	8.11	-0.13	32.01	31.93
175	0.47	1.01	8.16	-0.00	32.01	32.97
200	0.21	0.78	8.38	-0.97	32.12	31.99
225	0.89	0.18	8.40	-0.86	31.01	30.30

**Table 3 :** Determination of kinetic and thermodynamic parameters  $[k_{eq}]_{293K}^{Nit}$ ,  $[k_{eq}]_{313K}^{Nit}$ ,  $[\Delta H^\circ]_{293K-313K}^{Nit}$ ,  $[\Delta G^\circ]_{293K-313K}^{Nit}$ ,  $[\Delta S^\circ]_{293K}^{Nit}$ ,  $[\Delta S^\circ]_{313K}^{Nit}$  with the addition of various amount of salt  $([NO_3]_{eff})_{CaNO_3}$  as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$  and  $[T]_{313K}$ .

$\left([NO_3^-]_{eff}\right)_{CaNO_3}$	$[k_{eq}]_{293K}^{Nit}$	$[k_{eq}]_{313K}^{Nit}$	$[\Delta H^\circ]_{293K-313K}^{Nit}$	$[\Delta G^\circ]_{293K-313K}^{Nit}$	$[\Delta S^\circ]_{293K}^{Nit}$	$[\Delta S^\circ]_{313K}^{Nit}$
25	4.01	4.23	7.92	-6.31	17.63	17.52
50	3.87	3.91	8.11	-5.47	51.93	51.81
75	3.76	3.79	8.29	-1.41	48.06	37.93
100	3.11	3.18	8.68	-0.86	35.99	35.73
125	2.52	2.63	8.83	-0.98	31.82	31.54
150	2.08	2.26	8.99	-0.11	34.99	34.91
175	1.80	1.93	9.02	-0.01	34.98	34.66
200	1.01	1.63	9.05	-0.98	34.12	34.01
225	0.98	1.01	9.09	-0.85	29.93	29.62

**Table 4 :** Determination of statistical parameters of thermodynamic parameters  $[\Delta S^\circ]_{293K}^{Chl}$ ,  $[\Delta S^\circ]_{293K}^{Fl}$ ,  $[\Delta S^\circ]_{293K}^{Nit}$ ,  $[\Delta G^\circ]_{293K}^{Chl}$ ,  $[\Delta G^\circ]_{293K}^{Fl}$ ,  $[\Delta G^\circ]_{293K}^{Nit}$ ,  $[\Delta H^\circ]_{293K}^{Chl}$ ,  $[\Delta H^\circ]_{293K}^{Fl}$ ,  $[\Delta H^\circ]_{293K}^{Nit}$  with the addition of various amount of salt  $\left([Cl^-]_{eff}\right)_{CaCl_2}$ ,  $\left([F^-]_{eff}\right)_{CaF_2}$ ,  $\left([NO_3^-]_{eff}\right)_{CaNO_3}$  as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$ .

$\left([Ion]_{eff}\right)_{sal}$	$[\Delta H^\circ]_{293K}^{Chl}$	$[\Delta H^\circ]_{293K}^{Fl}$	$[\Delta H^\circ]_{293K}^{Nit}$	$[\Delta G^\circ]_{293K}^{Chl}$	$[\Delta G^\circ]_{293K}^{Fl}$	$[\Delta G^\circ]_{293K}^{Nit}$	$[\Delta S^\circ]_{293K}^{Chl}$	$[\Delta S^\circ]_{293K}^{Fl}$	$[\Delta S^\circ]_{293K}^{Nit}$
25	7.67	7.66	7.92	-6.09	-6.29	-6.31	16.53	15.52	17.63
50	7.62	7.63	8.11	-5.30	-5.46	-5.47	49.91	47.93	51.93
75	7.56	7.97	8.29	-1.28	-1.41	-1.41	36.06	35.01	33.06
100	7.87	7.86	8.68	-0.62	-0.81	-0.86	34.83	33.83	35.99
125	7.93	7.92	8.83	-0.67	-0.93	-0.98	31.80	30.80	31.82
150	8.12	8.11	8.99	-0.13	-0.13	-0.11	34.02	32.01	34.99
175	8.15	8.16	9.02	-0.00	-0.00	-0.01	34.63	33.01	34.98
200	8.39	8.38	9.05	-0.93	-0.97	-0.98	34.21	32.12	34.12
225	8.48	8.40	9.09	-0.82	-0.86	-0.85	33.02	31.01	29.93
Mean	7.98	8.01	8.66	-1.76	-1.87	-1.89	33.89	32.36	33.83
S.D.	0.33	0.28	0.45	2.273	2.32	2.32	8.44	8.22	8.78
R <sup>2</sup> (linear)	0.92	0.92	0.90	0.559	0.58	0.58	0.01	0.00	0.00
R <sup>2</sup> (Polynomial)	0.946	0.92	0.982	0.91	0.913	0.913	0.106	0.118	0.12

$[k_e]$  Equilibrium constant  $k_{eq} = \frac{[AC]_{aad}}{[AC]_{ad}} * \left([Cl^-]_{eff}\right)_{CaCl_2}$ ,  $\left([F^-]_{eff}\right)_{CaF_2}$ ,  $\left([NO_3^-]_{eff}\right)_{CaNO_3}$  Adsorbate in mg/gm \*  $[\Delta H^\circ]_{293K-313K}$  Enthalpy change in  $KJ mol^{-1}$  \*  $[\Delta G^\circ]_{293K-313K}$  Gibbs free energy change in  $KJ mol^{-1}$  \*  $[\Delta S^\circ]_{293K}$  Entropy change in  $JK^{-1}mol^{-1}$  at 293 K \*  $[\Delta S^\circ]_{313K}$  Entropy change in  $JK^{-1}mol^{-1}$  at 313 K

**Figure 1 :** Mathematical modeling and determination of thermodynamic parameters  $[\Delta S^\circ]_{293K}^{Chl}$ ,  $[\Delta S^\circ]_{293K}^{Fl}$ ,  $[\Delta S^\circ]_{293K}^{Nit}$ ,  $[\Delta G^\circ]_{293K}^{Chl}$ ,  $[\Delta G^\circ]_{293K}^{Fl}$ ,  $[\Delta G^\circ]_{293K}^{Nit}$ ,  $[\Delta H^\circ]_{293K}^{Chl}$ ,  $[\Delta H^\circ]_{293K}^{Fl}$ ,  $[\Delta H^\circ]_{293K}^{Nit}$  with the addition of various amount of salt  $\left([Cl^-]_{eff}\right)_{CaCl_2}$ ,  $\left([F^-]_{eff}\right)_{CaF_2}$ ,  $\left([NO_3^-]_{eff}\right)_{CaNO_3}$  as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$ .

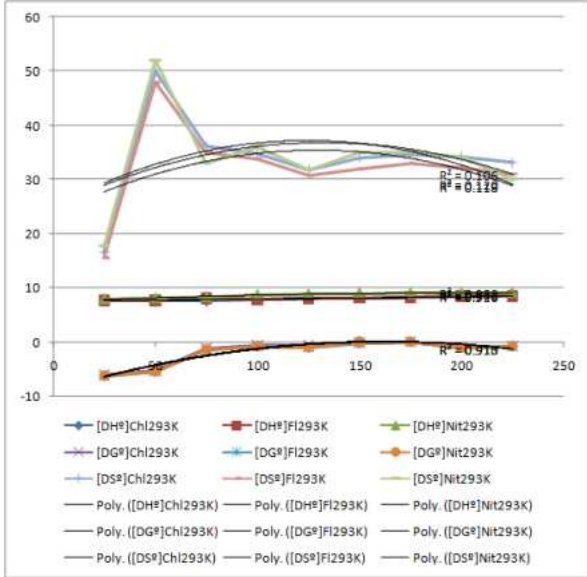
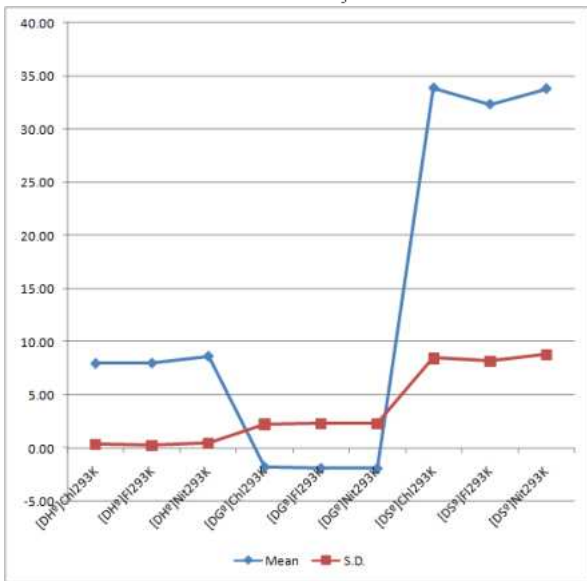


Figure 2 : Mathematical modeling and determination of thermodynamic parameters  $[\Delta S^\circ]_{293K}^{Chl}$ ,  $[\Delta S^\circ]_{293K}^{Fl}$ ,  $[\Delta S^\circ]_{293K}^{Nit}$ ,  $[\Delta G^\circ]_{293K}^{Chl}$ ,  $[\Delta G^\circ]_{293K}^{Fl}$ ,  $[\Delta G^\circ]_{293K}^{Nit}$ ,  $[\Delta H^\circ]_{293K}^{Chl}$ ,  $[\Delta H^\circ]_{293K}^{Fl}$ ,  $[\Delta H^\circ]_{293K}^{Nit}$  with the addition of various amount of salt  $([Cl^-]_{eff})_{CaCl_2}$ ,  $([F^-]_{eff})_{CaF_2}$ ,  $([NO_3^-]_{eff})_{CaNO_3}$  as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$ .



**Result and Discussion :**

In the reference of same counter ion mutually competitor ions  $Cl^-$ ,  $F^-$  and  $NO_3^-$  leaching kinetics and thermodynamics parameters and statistical values vary in the way of infacing or inhibitions to being adsorbed, retained as complexed or leached down in order to affect abicnds both biotic and nonbiotic factors in study region. Although leaching rate profiles  $[L_R]$  are sign of unadsorbed amount  $[AC]_{unad}$  and rest amount can be shown as adsorbed amount  $[AC]_{ad}$  including complexed form of ions like  $[Cl^-]_{compx}$ ,  $[F^-]_{compx}$ ,  $[NO_3^-]_{compx}$  but with the changing in a range of temp  $[T]_{273K-313K}$  and varying in effluents amount and concentration as  $([Cl^-]_{eff})_{CaCl_2}$ ,  $([F^-]_{eff})_{CaF_2}$ ,  $([NO_3^-]_{eff})_{CaNO_3}$  very amazing and interesting results were obtained. At the initial state reaction order  $[n]$ , rate constant  $[k]$ , equilibrium constant  $[k_{eq}]$  were obtained at formula base chemistry and reaction order was found fit in 1<sup>st</sup> order reaction. Further Gibbs free energy as  $[\Delta G^\circ]_{293K-313K}^{Chl}$ ,  $[\Delta G^\circ]_{293K-313K}^{Fl}$ ,  $[\Delta G^\circ]_{293K-313K}^{Nit}$  calculated on the behalf. Negative values of  $[\Delta G^\circ]$  indicate reaction during ions adsorption is how much spontaneous process. With increasing temperature adsorption was too found in increasing order as particles potential energy too increases thus cnthalpy changes as  $[\Delta H^\circ]_{293K-313K}^{Chl}$ ,  $[\Delta H^\circ]_{293K-313K}^{Fl}$ ,  $[\Delta H^\circ]_{293K-313K}^{Nit}$  were too noticed increasing because of endothermic

reaction, entropy changes as  $[\Delta S^{\circ}]_{293K}^{Chl}$ ,  $[\Delta S^{\circ}]_{293K}^{Fl}$ ,  $[\Delta S^{\circ}]_{293K}^{Nit}$ ,  $[\Delta S^{\circ}]_{313K}^{Chl}$ ,  $[\Delta S^{\circ}]_{313K}^{Fl}$ ,  $[\Delta S^{\circ}]_{313K}^{Nit}$ , were observed positive which indicate the randomness of unadsorbed part and slightly increasing of adsorbed part ratio. It is well known absolute. Entropy is not inversely proportional to absolute temperature which increases with temperature because of increasing atomic vibration and the disorder of system but change in entropy in a constant temperature heat transfer does make it seems like entropy is inversely proportional to temperature based on the equation, but it actually only means that the amount of entropy change is less at higher temperature for a given heat transfer according to formulae  $\Delta S^{\circ} = Q/T'$  if  $\Delta S^{\circ} = \Delta H^{\circ} - \Delta G^{\circ}/T$ . Mathematical modelling proves closeness of data to actual theory and equations. The positive values of mean observed as 7.98 for  $[\Delta H^{\circ}]_{293K}^{Chl}$ , 8.01 for  $[\Delta H^{\circ}]_{293K}^{Fl}$ , 8.66 for  $[\Delta H^{\circ}]_{293K}^{Nit}$ , and negative values for Gibbs free energy changes as -1.76 for  $[\Delta G^{\circ}]_{293K}^{Chl}$ , -1.87 for  $[\Delta G^{\circ}]_{293K}^{Fl}$ , -1.89 for  $[\Delta G^{\circ}]_{293K}^{Nit}$ , and high positive values for entropy changes as 33.89 for  $[\Delta S^{\circ}]_{293K}^{Chl}$ , 32.36 for  $[\Delta S^{\circ}]_{293K}^{Fl}$ , 33.83 for  $[\Delta S^{\circ}]_{293K}^{Nit}$ , while SD values differs as 0.33 for  $[\Delta H^{\circ}]_{293K}^{Chl}$ , 0.28 for  $[\Delta H^{\circ}]_{293K}^{Fl}$ , 0.45 for  $[\Delta H^{\circ}]_{293K}^{Nit}$ , 2.273 for  $[\Delta G^{\circ}]_{293K}^{Chl}$ , 2.32 for  $[\Delta G^{\circ}]_{293K}^{Fl}$ , 2.32 for  $[\Delta G^{\circ}]_{293K}^{Nit}$ , 8.44 for  $[\Delta S^{\circ}]_{293K}^{Chl}$ , 8.22 for  $[\Delta S^{\circ}]_{293K}^{Fl}$ , 8.78 for  $[\Delta S^{\circ}]_{293K}^{Nit}$  and  $R^2$  linear values were observed as 0.92 for  $[\Delta H^{\circ}]_{293K}^{Chl}$ , 0.92 for  $[\Delta H^{\circ}]_{293K}^{Fl}$ , 0.900 for  $[\Delta H^{\circ}]_{293K}^{Nit}$ , 0.559 for  $[\Delta G^{\circ}]_{293K}^{Chl}$ , 0.58 for  $[\Delta G^{\circ}]_{293K}^{Fl}$ , 0.58 for  $[\Delta G^{\circ}]_{293K}^{Nit}$ , 0.01 for  $[\Delta S^{\circ}]_{293K}^{Chl}$ , 0.00 for  $[\Delta S^{\circ}]_{293K}^{Fl}$ , 0.00 for  $[\Delta S^{\circ}]_{293K}^{Nit}$  and  $R^2$  polynomial values were observed as 0.946 for  $[\Delta H^{\circ}]_{293K}^{Chl}$ , 0.92 for  $[\Delta H^{\circ}]_{293K}^{Fl}$ , 0.982 for  $[\Delta H^{\circ}]_{293K}^{Nit}$ , 0.91 for  $[\Delta G^{\circ}]_{293K}^{Chl}$ , 0.913 for  $[\Delta G^{\circ}]_{293K}^{Fl}$ , 0.913 for  $[\Delta G^{\circ}]_{293K}^{Nit}$ , 0.106 for  $[\Delta S^{\circ}]_{293K}^{Chl}$ , 0.118 for  $[\Delta S^{\circ}]_{293K}^{Fl}$ , 0.12 for  $[\Delta S^{\circ}]_{293K}^{Nit}$  respectively shows closeness to actual data.

### Conclusion :

As negative charges being slightly bigger in size than positive ions but carrying equal single negative charge tend to minor slow down in leaching down because through soil profile abundant ions as  $Cl^-$ ,  $F^-$  and  $NO_3^-$ . Abundant ions as  $Cl^-$ ,  $F^-$  and  $NO_3^-$  in alkaline soil affect the leaching or absorbing factors of study area soil besides commenting mutually with other ions, the entire process of thermodynamic and kinetics studies of adsorption of ion may help to know ion adsorption and leaching efficiency in the soil medium in order to know retain or escaping capacities of metals in the soil and their contamination boundaries.

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