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## Mathematical kinetic and thermodynamic study of adsorption of competitor ion as calcium II, magnesium II and sodium I on alkaline soil using batch method

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### Abstract

Salinization of irrigation areas is a global environmental challenge. The uncertainty in the distribution of salinization is increased by the complexity of the natural environment. The environmental factors were found to control the distribution of salinization whereas human activity affected the degree of change in salinization. Soil salinization can be defined as the process of salt accumulation in the root zone of soil and can seriously affect the water transportation and growth of crops, thus limiting the agricultural potential of soil. In fact, salinization is a complex process influenced by many factors, which results in its significant spatial variations during experiments so in this way main purpose of this work is to comparatively study the adsorption of calcium, magnesium and sodium as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  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  $[k_{eq}]$ ,  $[\Delta H^\circ]$ ,  $[\Delta G^\circ]$ ,  $[\Delta S^\circ]$ . The series of experiments were done with different amount and concentrations of adsorbate or effluents as  $([Ca^{2+}]_{eff})_{CaCl_2}$ ,  $([Mg^{2+}]_{eff})_{MgCl_2}$ ,  $([Na^+]_{eff})_{NaCl}$  in the temperature range of 293K to 313K by using batch process method. Although rates of adsorption  $[Ad_R]$  or rates of unadsorption  $[Uad_R]$  were found almost 1<sup>st</sup> 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.

**Keywords:** Equilibrium constant, kinetic parameter, enthalpy changes, free energy changes, entropy changes, CCA

### Introduction

Soil and water salinity and associate problems are a major challenge for global food production strategies to cope with salinity include a better understanding of the impacts of temporal and spatial dynamics of salinity on soil water balances evapotranspiration and division optimal irrigation schedules and efficient methods <sup>[1-3]</sup>. Furthermore the salinized areas are increasing at a rate of 10% annually for various reasons, including low precipitation, high surface evaporation, weathering of native rocks, irrigation with saline water, and poor cultural practices <sup>[3-5]</sup>. It has been estimated that more than 50% of the arable land would be salinized by the year 2050 <sup>[5, 6]</sup>. Although canal area become more suffered from soil salinity because of water logging is mainly subjected to ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  exchange capacities abundant <sup>[7, 8]</sup>. in the particular area so having higher specific gravity  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{NaCl}$  salts were selected by adding different concentration with different amount of effluents as  $([Ca^{2+}]_{eff})_{CaCl_2}$ ,  $([Mg^{2+}]_{eff})_{MgCl_2}$ ,  $([Na^+]_{eff})_{NaCl}$  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>[9, 10]</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>[10, 11]</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

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process frequently [11-12]. 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 [5, 6]. 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 [6-7]. As temperature can make two type's 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 [9]. Thus enthalpy change  $[\Delta H^\circ]$  Gibbs free energy change  $[\Delta G^\circ]$  and entropy change  $[\Delta S^\circ]$  were too observed and calculated of each experiment to know whether the reactions are spontaneous or non-spontaneous or feasible.  $[\Delta G^\circ]$  was found negative [10] while  $[\Delta H^\circ]$  was distinct positive [11, 12]. 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  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  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  $([Ca^{2+}]_{eff})_{CaCl_2}$ ,  $([Mg^{2+}]_{eff})_{MgCl_2}$ ,  $([Na^+]_{eff})_{NaCl}$  were added in the temperature range of  $[T]_{293K}$  to  $[T]_{313K}$  according to Rajasthan climate.

In thermostat conditional concentration change of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  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's 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  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  adsorbed on adsorbent in mg.
- $[AC]_{uad}$  = Concentration of ions as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  unadsorbed on adsorbent in mg
- $[k_{eq}]_{293K}^{Cal}$  = Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 293K regards  $Ca^{2+}$
- $[k_{eq}]_{313K}^{Cal}$  = Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 313K regards  $Ca^{2+}$
- $[k_{eq}]_{293K}^{Mag}$  = Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 293K regards  $Mg^{2+}$
- $[k_{eq}]_{313K}^{Mag}$  = Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 313K regards  $Mg^{2+}$
- $[k_{eq}]_{293K}^{Sod}$  = Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 293K regards  $Na^+$
- $[k_{eq}]_{313K}^{Sod}$  = Equilibrium constant ie  $k_{eq} = \frac{[AC]_{uad}}{[AC]_{ad}}$  at 313K regards  $Na^+$
- $[T]_{293K}$  = Temperature of 293 K maintained during experimental work in kelvin.
- $[T]_{313K}$  = Temperature of 313 K maintained during experimental work in kelvin.
- $([Ca^{2+}]_{eff})_{CaCl_2}$  =  $Ca^{2+}$  salt added from the top of glass column as effluent or adsorbate mg/gm
- $([Mg^{2+}]_{eff})_{MgCl_2}$  =  $Mg^{2+}$  salt added from the top of glass column as effluent or adsorbate mg/gm
- $([Na^+]_{eff})_{NaCl}$  =  $Na^+$  salt added from the top of glass column as effluent or adsorbate mg/gm
- $[\Delta H^\circ]_{293K-313K}^{Cal}$  = Enthalpy change with the temperature, reference of  $Ca^{2+}$  change in kilo joule per mole  $KJmol^{-1}$
- $[\Delta H^\circ]_{293K-313K}^{Mag}$  = Enthalpy change with the temperature, reference of  $Mg^{2+}$  change in kilo joule per mole  $KJmol^{-1}$
- $[\Delta H^\circ]_{293K-313K}^{Sod}$  = Enthalpy change with the temperature, reference of  $Na^+$  change in kilo joule per mole  $KJmol^{-1}$
- $[\Delta G^\circ]_{293K-313K}^{Cal}$  = Gibbs free energy change with the temperature, reference of  $Ca^{2+}$  change in kilo joule per mole  $KJmol^{-1}$
- $[\Delta G^\circ]_{293K-313K}^{Mag}$  = Gibbs free energy change with the temperature, reference of  $Mg^{2+}$  change in kilo joule per mole  $KJmol^{-1}$
- $[\Delta G^\circ]_{293K-313K}^{Sod}$  = Gibbs free energy change with the temperature, reference of  $Na^+$  change in kilo joule per mole  $KJmol^{-1}$
- $[\Delta S^\circ]_{293K}^{Cal}$  = Entropy change with the 293 K temperature, reference of  $Ca^{2+}$  change in joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{293K}^{Mag}$  = Entropy change with the 293 K temperature, reference of  $Mg^{2+}$  change in joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{293K}^{Sod}$  = Entropy change with the 293 K temperature, reference of  $Na^+$  change in joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{313K}^{Cal}$  = Entropy change with the 313 K temperature, reference of  $Ca^{2+}$  change in Joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{313K}^{Mag}$  = Entropy change with the 313 K temperature, reference of  $Mg^{2+}$  change in Joule per kelvin per mole  $JK^{-1}mol^{-1}$
- $[\Delta S^\circ]_{313K}^{Sod}$  = Entropy change with the 313 K temperature, reference of  $Na^+$  change in Joule per kelvin per mole  $JK^{-1}mol^{-1}$

**Table 1:** Determination of kinetic and thermodynamic parameters  $[k_{eq}]_{293K}^{Cal}$ ,  $[k_{eq}]_{313K}^{Cal}$ ,  $[\Delta H^\circ]_{293K-313K}^{Cal}$ ,  $[\Delta G^\circ]_{293K-313K}^{Cal}$ ,  $[\Delta S^\circ]_{293K}^{Cal}$ ,  $[\Delta S^\circ]_{313K}^{Cal}$  with the addition of various amount of salt  $([Ca^{2+}]_{eff})_{CaCl_2}$  as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$  and  $[T]_{313K}$

$([Ca^{2+}]_{eff})_{CaCl_2}$	$[k_{eq}]_{293K}^{Cal}$	$[k_{eq}]_{313K}^{Cal}$	$[\Delta H^\circ]_{293K-313K}^{Cal}$	$[\Delta G^\circ]_{293K-313K}^{Cal}$	$[\Delta S^\circ]_{293K}^{Cal}$	$[\Delta S^\circ]_{313K}^{Cal}$
25	4.18	4.83	8.67	-7.09	17.53	17.50
50	4.00	4.27	8.62	-3.60	50.91	50.96
75	3.78	4.07	8.56	-2.28	37.06	37.02
100	3.26	3.71	8.87	-1.62	35.83	35.71
125	2.17	3.18	8.93	-0.67	32.80	32.73
150	2.01	2.52	9.12	-1.13	35.02	35.01
175	1.48	2.06	9.15	-1.00	35.63	35.62
200	1.27	1.88	9.39	-0.93	35.21	35.16
225	0.99	1.23	9.48	-0.82	34.02	33.02

**Table 2:** Determination of kinetic and thermodynamic parameters  $[k_{eq}]_{293K}^{Mag}$ ,  $[k_{eq}]_{313K}^{Mag}$ ,  $[\Delta H^\circ]_{293K-313K}^{Mag}$ ,  $[\Delta G^\circ]_{293K-313K}^{Mag}$ ,  $[\Delta S^\circ]_{293K}^{Mag}$ ,  $[\Delta S^\circ]_{313K}^{Mag}$  with the addition of various amount of  $([Mg^{2+}]_{eff})_{MgCl_2}$  as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$  and  $[T]_{313K}$ .

$([Mg^{2+}]_{eff})_{MgCl_2}$	$[k_{eq}]_{293K}^{Mag}$	$[k_{eq}]_{313K}^{Mag}$	$[\Delta H^\circ]_{293K-313K}^{Mag}$	$[\Delta G^\circ]_{293K-313K}^{Mag}$	$[\Delta S^\circ]_{293K}^{Mag}$	$[\Delta S^\circ]_{313K}^{Mag}$
25	4.11	4.81	8.66	-7.29	16.52	16.48
50	3.92	4.25	8.63	-6.46	48.93	48.76
75	3.70	4.01	8.97	-2.41	36.01	35.86
100	3.21	3.92	8.86	-1.81	34.83	34.70
125	2.10	3.52	8.92	-0.93	31.80	31.72
150	1.93	2.48	9.11	-0.13	33.01	32.93
175	1.47	2.01	9.16	-1.00	34.01	33.97
200	1.21	1.78	9.38	-0.97	33.12	32.99
225	0.89	1.18	9.40	-0.86	32.01	31.30

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

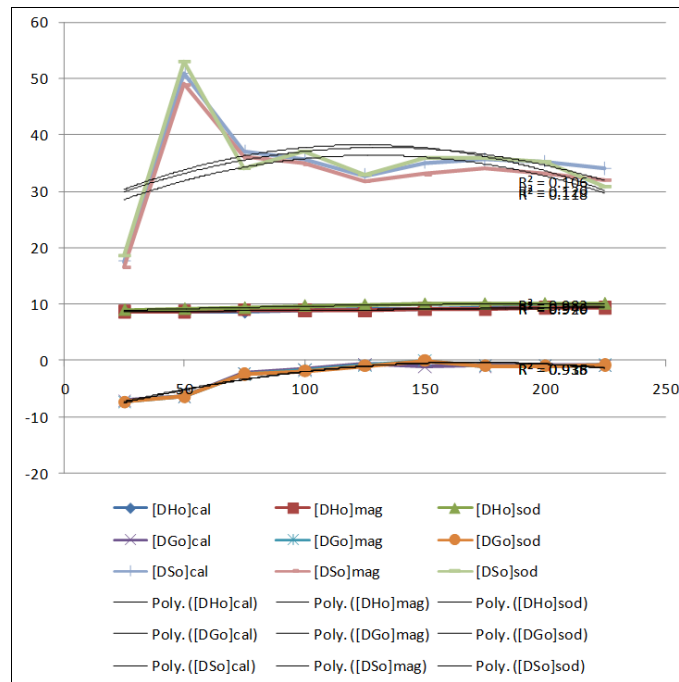
$([Na^+]_{eff})_{NaCl}$	$[k_{eq}]_{293K}^{Sod}$	$[k_{eq}]_{313K}^{Sod}$	$[\Delta H^\circ]_{293K-313K}^{Sod}$	$[\Delta G^\circ]_{293K-313K}^{Sod}$	$[\Delta S^\circ]_{293K}^{Sod}$	$[\Delta S^\circ]_{313K}^{Sod}$
25	5.01	5.23	8.92	-7.31	18.63	18.52
50	4.87	4.91	9.11	-6.47	52.93	52.81
75	4.76	4.79	9.29	-2.41	49.06	38.93
100	4.11	4.18	9.68	-1.86	36.99	36.73
125	3.52	3.63	9.83	-0.98	32.82	32.54
150	3.08	3.26	9.99	-0.11	35.99	35.91
175	2.80	2.93	10.02	-1.01	35.98	35.66
200	2.01	2.63	10.05	-0.98	35.12	35.01
225	1.98	2.01	10.09	-0.85	30.93	30.62

**Table 4 :** Determination of statistical parameters of thermodynamic parameters  $[\Delta S^\circ]_{293K}^{Cal}$ ,  $[\Delta S^\circ]_{293K}^{Mag}$ ,  $[\Delta S^\circ]_{293K}^{Sod}$ ,  $[\Delta G^\circ]_{293K}^{Cal}$ ,  $[\Delta G^\circ]_{293K}^{Mag}$ ,  $[\Delta G^\circ]_{293K}^{Sod}$ ,  $[\Delta H^\circ]_{293K}^{Cal}$ ,  $[\Delta H^\circ]_{293K}^{Mag}$ ,  $[\Delta H^\circ]_{293K}^{Sod}$  with the addition of various amount of salt  $([Ca^{2+}]_{eff})_{CaCl_2}$ ,  $([Mg^{2+}]_{eff})_{MgCl_2}$ ,  $([Na^+]_{eff})_{NaCl}$ , as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$ .

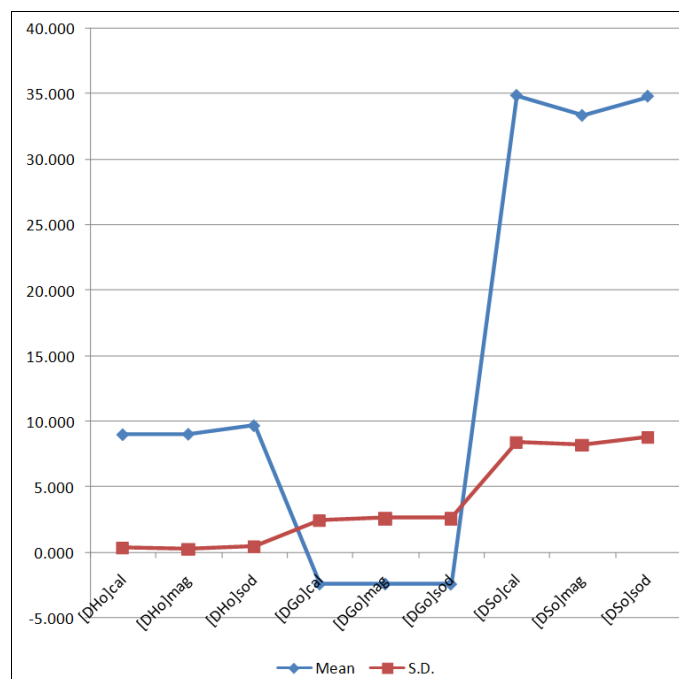
$([Ion]_{eff})_{sal}$	$[\Delta H^\circ]_{cal}$	$[\Delta H^\circ]_{mag}$	$[\Delta H^\circ]_{sod}$	$[\Delta G^\circ]_{cal}$	$[\Delta G^\circ]_{mag}$	$[\Delta G^\circ]_{sod}$	$[\Delta S^\circ]_{cal}$	$[\Delta S^\circ]_{mag}$	$[\Delta S^\circ]_{sod}$
25	8.67	8.66	8.92	-7.09	-7.29	-7.31	17.53	16.52	18.63
50	8.62	8.63	9.11	-6.30	-6.46	-6.47	50.91	48.93	52.93
75	8.56	8.97	9.29	-2.28	-2.41	-2.41	37.06	36.01	34.06
100	8.87	8.86	9.68	-1.62	-1.81	-1.86	35.83	34.83	36.99
125	8.93	8.92	9.83	-0.67	-0.93	-0.98	32.80	31.80	32.82
150	9.12	9.11	9.99	-1.13	-0.13	-0.11	35.02	33.01	35.99
175	9.15	9.16	10.02	-1.00	-1.00	-1.01	35.63	34.01	35.98
200	9.39	9.38	10.05	-0.93	-0.97	-0.98	35.21	33.12	35.12
225	9.48	9.40	10.09	-0.82	-0.86	-0.85	34.02	32.01	30.93

Mean	8.977	9.010	9.664	-2.427	-2.429	-2.442	34.89	33.360	34.82
S.D.	0.332	0.279	0.446	2.476	2.608	2.612	8.436	8.216	8.784
R <sup>2</sup> (linear)	0.919	0.916	0.900	0.665	0.668	0.671	0.007	0.002	0.000
R <sup>2</sup> (Polynomial)	0.946	0.92	0.982	0.918	0.936	0.935	0.106	0.118	0.12

$[k_e]$  Equilibrium constant  $k_{eq} = \frac{[AC]_{aad}}{[AC]_{ad}} * ([Ca^{2+}]_{eff})_{CaCl_2}, ([Mg^{2+}]_{eff})_{MgCl_2}, ([Na^+]_{eff})_{NaCl}$  Adsorbate in mg/gm \*  $[\Delta H^\circ]_{293K-313K}$  Enthalpy change in  $KJmol^{-1}$  \*  $[\Delta G^\circ]_{293K-313K}$  Gibbs free energy change in  $KJmol^{-1}$  \*  $[\Delta S^\circ]_{293K}$  Entropy change in  $JK^{-1}mol^{-1}$  at 293 K \*  $[\Delta S^\circ]_{313K}$  Entropy change in  $JK^{-1}mol^{-1}$  at 313 K



**Fig 1:** Mathematical modeling and determination of thermodynamic parameters  $[\Delta S^\circ]_{293K}^{Cal}, [\Delta S^\circ]_{293K}^{Mag}, [\Delta S^\circ]_{293K}^{Sod}, [\Delta G^\circ]_{293K}^{Cal}, [\Delta G^\circ]_{293K}^{Mag}, [\Delta G^\circ]_{293K}^{Sod}, [\Delta H^\circ]_{293K}^{Cal}, [\Delta H^\circ]_{293K}^{Mag}, [\Delta H^\circ]_{293K}^{Sod}$  with the addition of various amount of salt  $([Ca^{2+}]_{eff})_{CaCl_2}, ([Mg^{2+}]_{eff})_{MgCl_2}, ([Na^+]_{eff})_{NaCl}$ , as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$ .



**Fig 2:** Mathematical modeling and determination of thermodynamic parameters  $[\Delta S^\circ]_{293K}^{Cal}, [\Delta S^\circ]_{293K}^{Mag}, [\Delta S^\circ]_{293K}^{Sod}, [\Delta G^\circ]_{293K}^{Cal}, [\Delta G^\circ]_{293K}^{Mag}, [\Delta G^\circ]_{293K}^{Sod}, [\Delta H^\circ]_{293K}^{Cal}, [\Delta H^\circ]_{293K}^{Mag}, [\Delta H^\circ]_{293K}^{Sod}$  with the addition of various amount of salt  $([Ca^{2+}]_{eff})_{CaCl_2}$ ,

$([Mg^{2+}]_{eff})_{MgCl_2}$ ,  $([Na^+]_{eff})_{NaCl}$ , as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature  $[T]_{293K}$ .

## Results and Discussion

Being lighter positive ions leach down easily but may be effected by counter ion, their categories even other competitor positive ions showing affinity same or different with counter ion in order to affect CEC as cation exchange capacity and AEC as anion exchange capacity. 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 complexes form of ions like  $[Ca^{2+}]_{comp}$ ,  $[Mg^{2+}]_{comp}$ ,  $[Na^+]_{comp}$  but with the changing in a range of temp  $[T]_{273K-313K}$  and varying in effluents amount and concentration as  $([Ca^{2+}]_{eff})_{CaCl_2}$ ,  $([Mg^{2+}]_{eff})_{MgCl_2}$  and  $([Na^+]_{eff})_{NaCl}$  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  $[\Delta G^{\circ}]_{293K-313K}^{Cal}$ ,  $[\Delta G^{\circ}]_{293K-313K}^{Mag}$ ,  $[\Delta G^{\circ}]_{293K-313K}^{Sod}$  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 enthalpy changes as  $[\Delta H^{\circ}]_{293K-313K}^{Cal}$ ,  $[\Delta H^{\circ}]_{293K-313K}^{Mag}$ ,  $[\Delta H^{\circ}]_{293K-313K}^{Sod}$  were too noticed increasing because of endothermic reaction, entropy changes as  $[\Delta S^{\circ}]_{293K}^{Cal}$ ,  $[\Delta S^{\circ}]_{293K}^{Mag}$ ,  $[\Delta S^{\circ}]_{293K}^{Sod}$ ,  $[\Delta S^{\circ}]_{313K}^{Cal}$ ,  $[\Delta S^{\circ}]_{313K}^{Mag}$ ,  $[\Delta S^{\circ}]_{313K}^{Sod}$  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 8.977 for  $[\Delta H^{\circ}]_{293K}^{Cal}$ , 9.010 for  $[\Delta H^{\circ}]_{293K}^{Mag}$ , 9.664 for  $[\Delta H^{\circ}]_{293K}^{Sod}$ , and negative values for Gibbs free energy changes as -2.427 for  $[\Delta G^{\circ}]_{293K}^{Cal}$ , -2.429 for  $[\Delta G^{\circ}]_{293K}^{Mag}$ , -2.442 for  $[\Delta G^{\circ}]_{293K}^{Sod}$ , and high positive values for entropy changes as 34.89 for  $[\Delta S^{\circ}]_{293K}^{Cal}$ , 33.36 for  $[\Delta S^{\circ}]_{293K}^{Mag}$ , 34.82 for  $[\Delta S^{\circ}]_{293K}^{Sod}$ , while SD values differs as 0.332 for  $[\Delta H^{\circ}]_{293K}^{Cal}$ , 0.272 for  $[\Delta H^{\circ}]_{293K}^{Mag}$ , 0.4464 for  $[\Delta H^{\circ}]_{293K}^{Sod}$ , 2.476 for  $[\Delta G^{\circ}]_{293K}^{Cal}$ , 2.608 for  $[\Delta G^{\circ}]_{293K}^{Mag}$ , 2.6124 for  $[\Delta G^{\circ}]_{293K}^{Sod}$ , 8.436 for  $[\Delta S^{\circ}]_{293K}^{Cal}$ , 8.216 for  $[\Delta S^{\circ}]_{293K}^{Mag}$ , 8.784 for  $[\Delta S^{\circ}]_{293K}^{Sod}$  and  $R^2$  linear values were observed as 0.919 for  $[\Delta H^{\circ}]_{293K}^{Cal}$ , 0.916 for  $[\Delta H^{\circ}]_{293K}^{Mag}$ , 0.900 for  $[\Delta H^{\circ}]_{293K}^{Sod}$ , 0.665 for  $[\Delta G^{\circ}]_{293K}^{Cal}$ , 0.668 for  $[\Delta G^{\circ}]_{293K}^{Mag}$ , 0.671 for  $[\Delta G^{\circ}]_{293K}^{Sod}$ , 0.007 for  $[\Delta S^{\circ}]_{293K}^{Cal}$ , 0.002 for  $[\Delta S^{\circ}]_{293K}^{Mag}$ , 0.001 for  $[\Delta S^{\circ}]_{293K}^{Sod}$  and  $R^2$  polynomial values were observed as 0.946 for  $[\Delta H^{\circ}]_{293K}^{Cal}$ , 0.920 for  $[\Delta H^{\circ}]_{293K}^{Mag}$ , 0.982 for  $[\Delta H^{\circ}]_{293K}^{Sod}$ , 0.918 for  $[\Delta G^{\circ}]_{293K}^{Cal}$ , 0.936 for  $[\Delta G^{\circ}]_{293K}^{Mag}$ , 0.935 for  $[\Delta G^{\circ}]_{293K}^{Sod}$ , 0.106 for  $[\Delta S^{\circ}]_{293K}^{Cal}$ , 0.118 for  $[\Delta S^{\circ}]_{293K}^{Mag}$ , 0.12 for  $[\Delta S^{\circ}]_{293K}^{Sod}$  respectively shows closeness to actual data.

## Conclusion

Abundant ions as  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+$  in alkaline soil affect the leaching or absorbing factors of study area soil besides commentating 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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