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Mathematical kinetic and thermodynamic study of adsorption of chloride I by alkaline soil using batch method

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Abstract

In alkaline soil chloride ion may be as counter ion of calcium and sodium while may be in excess because of water logging and because of input intentionally and having high anion exchange capacity in most of study area. It may be high or low leached or not in order to affect the quality of soil, surface water and ground water. In this way the aim of this work was to study the adsorption of Cl^- on the soil sample [ss] with different amount of adsorbate $\left([Cl^-]_{eff}\right)_{MgCl_2}$ in the temperature range of 293K to 313K by using batch process method. Rate of adsorption was found nearest to 1st order reaction. Adsorption and desorption process run as complementary process gave equilibrium constant k_e which tends to give approach of thermodynamics parameters like enthalpy change, Gibbs free energy change, entropy changes respectively $[\Delta H^\circ]$, $[\Delta G^\circ]$, $[\Delta S^\circ]$ with the help of mathematical modeling the kinetics and thermodynamic parameter were interpreted to make ease to understood with clear predictions, distribution classification and assumptions of the entire data's mutual relation.

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

Introduction

Although study area is affected with alkalinity but the salinity buildup also vary with soil type ^[1-4]. Besides excess of chloride ion input can be leached down easily ^[5-6]. In area where rainfall is low, soil leaching is usually insufficient to completely remove salts from soil profiles and may be concentrated more by evapotranspiration processes ^[7-8]. Alkali soils owe their unfavorable physico-chemical properties mainly to the dominating presence of particular salt which causes the soil to swell and difficult to clarify or settle ^[9-10]. Although chloride plays important role in anion exchange capacity and because of its small size it is easily leached consequently affecting the quality of soil and ground water even surface water ^[11, 12]. So it was keened to study the chloride leaching kinetics and thermodynamics factors to clarify the adsorption or desorption of ion having relation with cofactors like other counter ions, competitor ions, climatic or seasonally changes or temperature changes ^[5, 6]. A very abundant salt $MgCl_2$ was selected to study the adsorption or desorption process through the glass column method and using by batch process method. 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 sodium adsorption kinetic studies were done which describe residential or uptake time of solute on solvent at the solid solution interface ^[3, 4]. The kinetical parameters can scale up studies of soil remediation process connecting optimum operational conditions of chloride predicting by important directional or non-directional operations of the ion adsorption and remedial operations ^[4-6]. 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

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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⁾.

Materials and Methods

For the estimation of chloride $[Cl^-]$ 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 $\left([Cl^-]_{eff}\right)_{MgCl_2}$ were added in the temperature range of $[T]_{293K}$ to $[T]_{313K}$ according to Rajasthan climate.

In thermostat conditional concentration change of $[Cl^-]$ was noticed and with the help of adsorbed amount of sodium

$[AC]_{ad}$ and unadsorbed amount of sodium $[AC]_{uad}$, equilibrium constant $k_e = \frac{k_{ad}}{k_{uad}} = \frac{[AC]_{uad}}{[AC]_{ad}}$ 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

$\Delta G^\circ = -RT \ln k_e$, ΔS° 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 $[Cl^-]$ adsorbed on adsorbent in mg.

$[AC]_{uad}$ = Concentration of $[Cl^-]$ unadsorbed on adsorbent in mg

k_e = Equilibrium constant ie $k_e = \frac{[AC]_{uad}}{[AC]_{ad}}$

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

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

$\left([Cl^-]_{eff}\right)_{MgCl_2}$ = Chloride salt added from the top of glass column as effluent or adsorbate mg/gm

$[\Delta H^\circ]_{293K-313K}$ = Enthalpy change with the temperature, change in kilo joule per mole $KJmol^{-1}$

$[\Delta G^\circ]_{293K-313K}$ = Gibbs free energy change with the temperature change in kilo joule per mole $KJmol^{-1}$.

$[\Delta S^\circ]_{293K}$ = Entropy change with the 293 K temperature in joule per kelvin per mole $JK^{-1}mol^{-1}$

$[\Delta S^\circ]_{313K}$ = Entropy change with the 313 K temperature in Joule per kelvin per mole $JK^{-1}mol^{-1}$

Table 1: Determination of Kinetic and thermodynamic parameters k_e , $[\Delta H^\circ]_{293K-313K}$, $[\Delta G^\circ]_{293K-313K}$, $[\Delta S^\circ]_{293K}$, $[\Delta S^\circ]_{313K}$, with the addition of various amount of salt $\left([Cl^-]_{eff}\right)_{MgCl_2}$ as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature $[T]_{293K}$ and $[T]_{313K}$.

$\left([Cl^-]_{eff}\right)_{MgCl_2}$	$[k_{eq}]_{293K}$	$[k_{eq}]_{313K}$	$[\Delta H^\circ]_{293K-313K}$	$[\Delta G^\circ]_{293K-313K}$	$[\Delta S^\circ]_{293K}$	$[\Delta S^\circ]_{313K}$
53.18	10.21	7.92	11.66	-15.05	21.50	20.30
70.90	6.13	36.08	11.58	-9.29	53.90	50.65
88.63	4.64	6.33	11.54	-5.28	40.05	37.6
106.35	4.10	5.08	11.83	-4.61	38.79	36.50
124.08	3.84	4.44	11.92	-3.67	35.80	33.71
141.80	3.69	4.11	12.11	-4.12	38.03	35.81
159.53	3.58	3.91	12.12	-4.01	38.62	36.36
177.25	3.51	3.78	12.1	-3.91	38.22	35.97
194.98	3.43	3.67	12.32	-3.83	37.6	35.55
212.70	3.41	3.59	12.46	-3.77	38.06	35.81
Mean	4.654	7.891	11.964	-4.721	38.057	35.826
S.D.	2.120	10.001	0.312	1.786	7.712	7.221
R ² (linear)	0.573	0.269	0.912	0.493	0.004	0.005
R ² (Polynomial)	0.865	0.318	0.919	0.06	0.064	0.065

k_e Equilibrium constant $k_e = \frac{[AC]_{uad}}{[AC]_{ad}} * \left([Cl^-]_{eff}\right)_{MgCl_2}$ 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

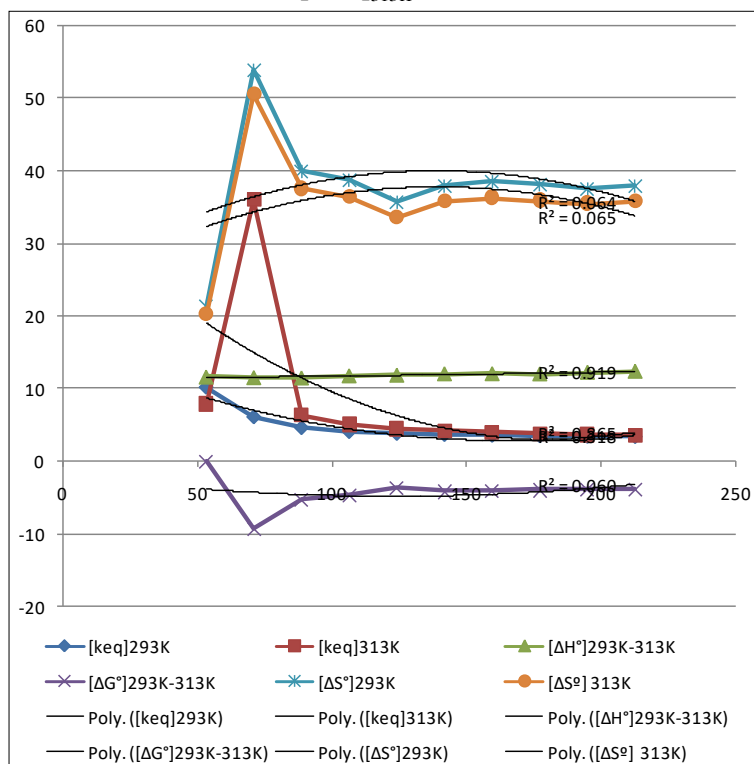


Fig 1: Mathematical modeling and determination of kinetic and thermodynamic parameters

k_e , $[\Delta H^\circ]_{293K-313K}$, $[\Delta G^\circ]_{293K-313K}$, $[\Delta S^\circ]_{293K}$, $[\Delta S^\circ]_{313K}$, with the addition of various amount of salt $\left([Cl^-]_{eff}\right)_{MgCl_2}$ as adsorbate on the soil sample [SS] as the adsorbent in the range of temperature $[T]_{293K}$ and $[T]_{313K}$.

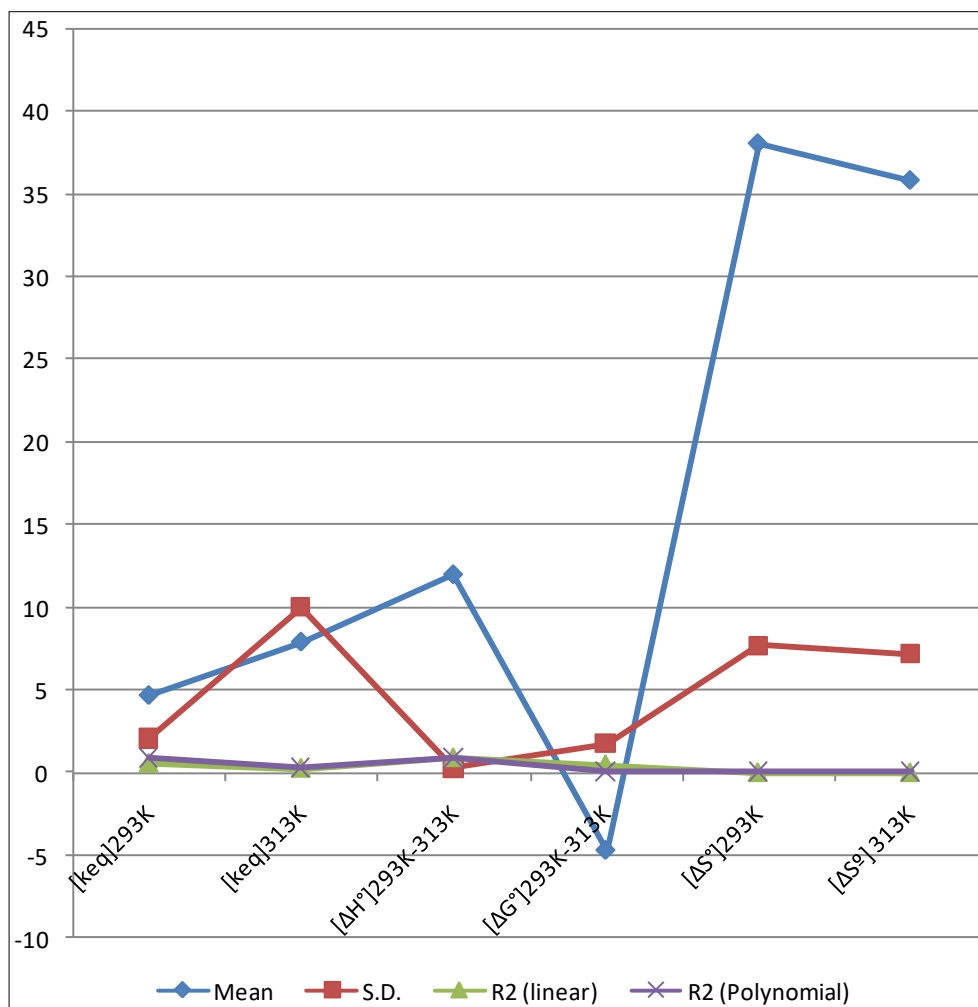


Fig 2: Mathematical modeling and determination of kinetic and thermodynamic parameters

k_e , $[\Delta H^\circ]_{293K-313K}$, $[\Delta G^\circ]_{293K-313K}$, $[\Delta S^\circ]_{293K}$, $[\Delta S^\circ]_{313K}$, with the addition of various amount of salt $\left([Cl^-]_{eff}\right)_{MgCl_2}$ as absorbate on the soil sample as the adsorbent in the range of temperature $[T]_{293K}$ and $[T]_{313K}$

Results and Discussion

A small sized ion with qualities of high AEC or high abundance in study area or high connectivity with small sized counter ions, very interesting results were obtained during entire work process of adsorption of chloride during a temperature range with changing in adsorbate quantity. Equilibrium constant k_e were calculated of each experiment and further Gibbs free energy $[\Delta G^\circ]$ calculated on the behalf. Negative values of $[\Delta G^\circ]$ indicate reaction during chloride 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 were too noticed increasing because of endothermic reaction entropy changes 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 4.654 for $[k_{eq}]_{293K}$, 7.891 for $[k_{eq}]_{313K}$, 11.964 for $[\Delta H^\circ]_{293K-313K}$, 38.057 for $[\Delta S^\circ]_{293K}$, 35.826 for $[\Delta S^\circ]_{313K}$, -4.721 for $[\Delta G^\circ]_{293K-313K}$ and negative value -0.153 for $[\Delta S^\circ]_{293K-313K}$ were observed while SD as 2.120, 10.001, 0.312, 1.786, 7.712, 7.221 R^2 (linear) as 0.573, 0.269, 0.912, 0.493, 0.004, 0.005 R^2 (Polynomial) as 0.865, 0.318, 0.919, 0.06, 0.064, 0.065 for $[k_{eq}]_{293K}$, $[k_{eq}]_{313K}$, $[\Delta H^\circ]_{293K-313K}$, $[\Delta G^\circ]_{293K-313K}$, $[\Delta S^\circ]_{293K}$, $[\Delta S^\circ]_{313K}$, respectively shows closeness to actual data.

Conclusion

Leaching or adsorbing power of alkaline soil of study area due the distinct variability with variety of abundant 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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