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Mathematical thermodynamic study of adsorption of calcium II by alkaline soil using batch method

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Abstract
The soil and water qualities besides related cofactors are affected by long or instantaneous time inputs on soil which directly depends upon the adsorption capacity of metal either onto the soil or leaching from soil. In this way the aim of this work was to study the adsorption of Ca^{2+} on to the soil sample [ss] with different amount of adsorbate in the temperature range of 293K to 313K by using batch process method. Rate of adsorption was found nearest to Ist 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 $[\Delta H^o], [\Delta G^o], [\Delta S^o]$ 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, free energy, entropy

Introduction
The alkaline soil around Kota city is facing the problem of Kota stone slurry, fly ash abundance, water hardness, metal pollution in water and & soil contamination due to adsorption, desorption and accumulation capacity of metal. Although calcium most probably found in the insoluble complex form but due to command area the soil salt problem is general thus for kinetics and thermodynamic studies of adsorption of calcium on the soil, easily soluble in water and having a higher specific gravity $CaCl_2$ salt was selected [1-3] and 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 calcium adsorption kinetic studies were done which describe residential or uptake time of solute on solvent at the solid solution interface [4, 5]. The kinetical parameters can scale up studies of soil remediation process connecting optimum operational conditions of calcium (II) predicting by important directional or non-directional operations of the ion adsorption and remedial operations [6-9]. 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 [10]. Thus enthalpy change $[\Delta H^o]$ Gibbs free energy change $[\Delta G^o]$ and entropy change $[\Delta S^o]$ were too observed and calculated of each experiment to know whether the reactions are spontaneous or non-spontaneous or feasible. $[\Delta G^o]$ was found negative [11] while $[\Delta H^o]$ was distinct positive [12].

Material and Methods
For the estimation of calcium $[Ca^{2+}]$ 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 60 cm and diameter of 3cm of glass column was prepared and gently packed or filled with 60 gm soil.

A fixed amount of salt as effluent $\left[Ca^{2+}\right]_{eff}$ were added in the temperature range of $[T]_{293K}$ to $[T]_{313K}$ according to Rajasthan climate.

In thermostate conditional concentration change of $\left[Ca^{2+}\right]$ was noticed and with the help of adsorbed amount of calcium $[AC]_{ad}$ and unadsorbed amount of calcium $[AC]_{uad}$, equilibrium constant $k_e = \frac{k_{ad}}{k_{uad}} = \frac{[AC]_{uad}}{[AC]_{ad}}$ were noticed for further kinetics and thermodynamics studies enthalpy $[\Delta H^o]$ by van't hoff equation $\frac{d \ln k}{dT} = \frac{\Delta H^o}{RT^2}$ or $\ln\left(\frac{k_2}{k_1}\right) = \frac{\Delta H^o}{8.314}\left(\frac{T_2 - T_1}{T_1\ T_2}\right)$

Gibbs energy by the following equations

$\Delta G^o = -RT \ln k_e$, ΔS^o by the following equation $\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}$ were calculated consequently in order to know reaction feasibility or spontanity.

The treatment of calculation of obtained data is based on the some parameter as defined below.

$[SS]$ = Soil sample

$[AC]_{ad}$ = Concentration of $\left[Ca^{2+}\right]$ adsorbed on adsorbent in mg.

$[AC]_{rad}$ = Concentration of $\left[Ca^{2+}\right]$ 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.

$\left(\left[Ca^{2+}\right]_{eff}\right)CaCl_2$ = Calcium salt added from the top of glass column as effluent or adsorbate mg/gm

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

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

$[\Delta S^o]_{293K}$ = Entropy change with the 293 K temperature in joul per kelvin per mole $JK^{-1}mol^{-}$ $[\Delta S^o]_{313K}$ = Entropy change with the 313 K temperature in Joul per kelvin per mole $JK^{-1}mol^{-}$

Table 1: Determination of Kinetic and thermodynamic parameters K_e, $[\Delta H^o]_{293K-313K}$, $[\Delta G^o]_{293K-313K}$, $[\Delta S^o]_{293K}$, $[\Delta S^o]_{313K}$, with the addition of various amount of salt $\left(\left[Ca^{2+}\right]_{eff}\right)CaCl_2$ as absorbate on the soil sample [SS] as the adsorbent in the range of temperature $[T]_{293K}$ and $[T]_{313K}$

$([Cl^-]_{eff})_{CaCl2}$	$[K_{eq}]_{293K}$	$[K_{eq}]_{313K}$	$[\Delta H°]_{293K\text{-}313K}$	$[\Delta G°]_{293K\text{-}313K}$	$[\Delta S°]_{293K}$	$[\Delta S°]_{313K}$
60.12	48.23	4.94	8.68	14.09	-18.51	-17.32
80.16	3.15	33.11	8.61	-6.31	50.92	47.67
100.2	1.66	3.37	8.57	-2.29	37.07	34.7
120.24	1.13	2.1	8.86	-1.63	35.81	33.52
140.28	0.87	1.47	8.94	-0.68	32.82	30.72
160.32	0.71	1.13	9.13	-1.14	35.06	32.82
180.36	0.61	0.93	9.14	-1.01	35.65	33.37
200.4	0.53	0.79	9.4	-0.92	35.25	32.99
220.43	0.47	0.69	9.34	-0.85	34.8	32.57
240.47	0.43	0.61	9.48	-0.79	35.07	32.83
Mean	5.779	4.914	9.015	-0.153	31.394	29.387
S.D.	14.1719	9.49075	0.31667807	5.009852393	17.3117	16.2034
R^2 (linear)	0.3142	0.00272	0.28133686	0.017471562	0.99552	1
R^2 (Polynomial)	0.621	0.319	0.927	0.304	0.341	0.341

k_e Equilibrium constant $k_e = \frac{[AC]_{rad}}{[AC]_{ad}} * \left(\left[Ca^{2+}\right]_{eff}\right)_{CaCl_2}$ Adsorbate in mg/gm.

$*\ [\Delta H^o]_{293K-313K}$ Enthalpy change in $KJ\ mol^{-1}$ $*\ [\Delta G^o]_{293K-313K}$ Gibbs free energy change in $KJ\ mol^{-1}$ $*\ [\Delta S^o]_{293K}$ Entropy change in $JK^{-1}mol^{-1}$ at 293 K $*\ [\Delta S^o]_{313K}$ Entropy change in $JK^{-1}mol^{-1}$ at 313 K

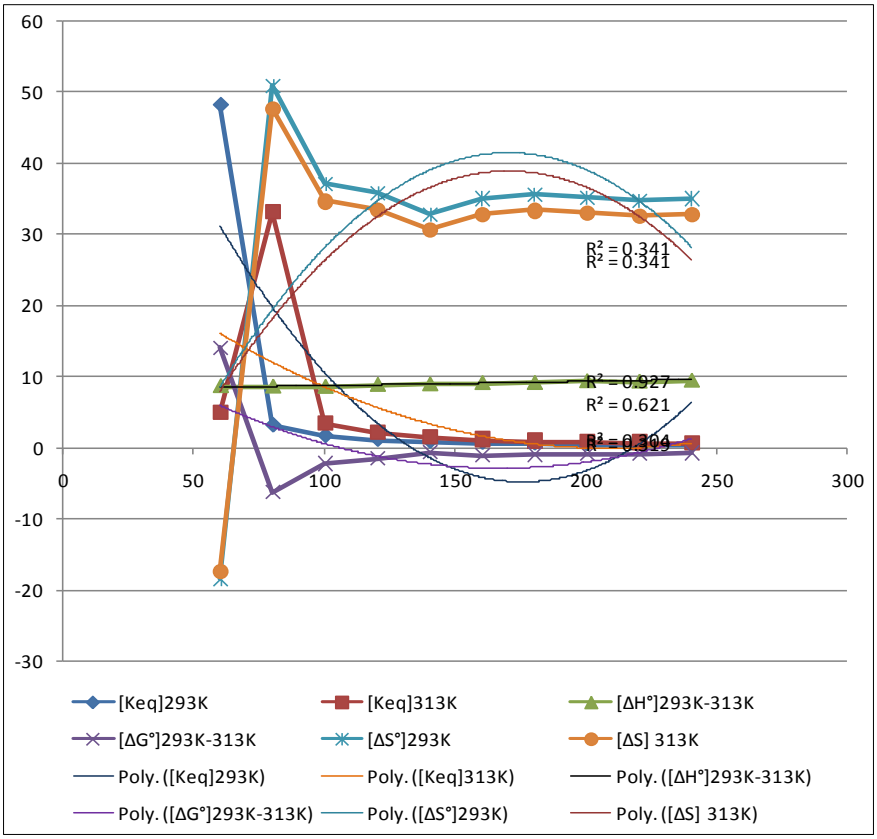

Fig 1: Mathematical modeling and determination of kinetic and thermodynamic parameters K_e, $[\Delta H^o]_{293K-313K}$, $[\Delta G^o]_{293K-313K}$, $[\Delta S^o]_{293K}$, $[\Delta S^o]_{313K}$, with the addition of various amount of salt $\left(\left[Ca^{2+}\right]_{eff}\right)CaCl_2$ as absorbate on the soil sample [SS] as the adsorbent in the range of temperature $[T]_{293K}$ and $[T]_{313K}$.

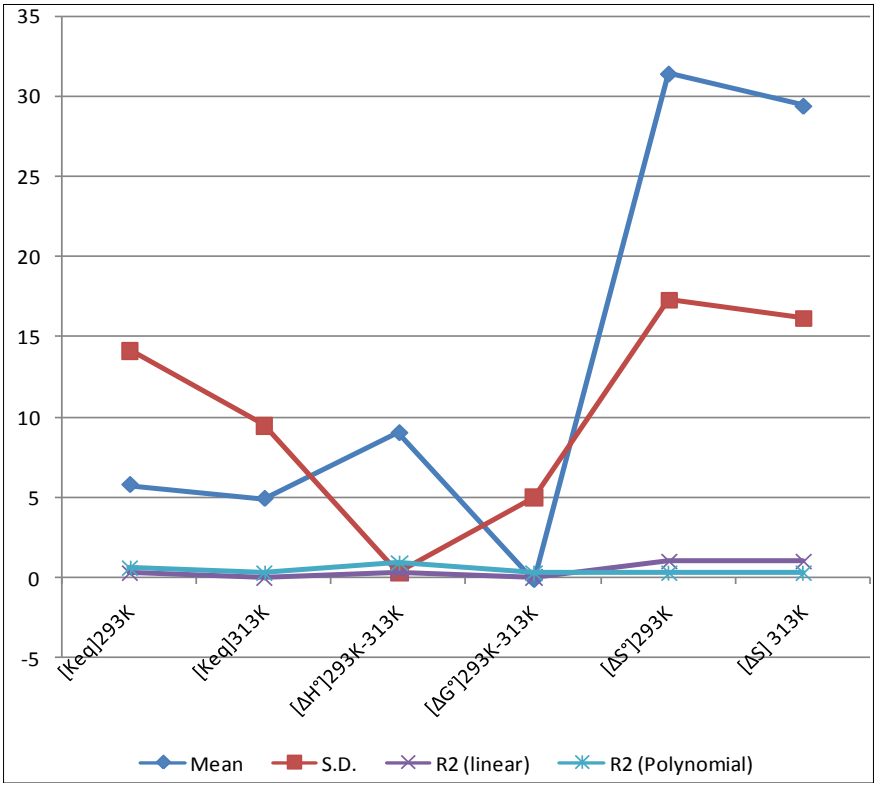

Fig 2: Mathematical modeling and determination of kinetic and thermodynamic parameters K_e, $[\Delta H^o]_{293K-313K}$, $[\Delta G^o]_{293K-313K}$, $[\Delta S^o]_{293K}$, $[\Delta S^o]_{313K}$, with the addition of various amount of salt $\left(\left[Ca^{2+}\right]_{eff}\right)CaCl_2$ as absorbate on the soil sample as the adsorbent in the range of temperature $[T]_{293K}$ and $[T]_{313K}$.

Results and Discussion

Very interesting results were obtained during entire work process of adsorption of Ca II during a temperature range with changing in adsorbate quantity. Equilibrium constant k_e were calculated of each experiment and further Gibbs free energy $[\Delta G^o]$ calculated on the behalf. Negative values of $[\Delta G^o]$ indicate reaction during Ca II 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 slighlty 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 $\Delta S^o = Q/T$ if $\Delta S^o = \Delta H^o - \Delta G^o/T$. Mathematical modelling proves closness of data to actual theory and equations.

The positive values of mean observed as 5.779 for $[K_{eq}]_{293K}$, 4.914 for $[K_{eq}]_{313K}$, 9.015 for $[\Delta H^o]_{293K-313K}$, 31.394 for $[\Delta S^o]_{293K}$, 29.387 for $[\Delta S^o]_{313K}$ and negative value –0.153 for $[\Delta S^o]_{293K-313K}$ were observed while SD as 14.1719, 9.49075, 0.36166, 5.0098, 17.3117, 16.2034 R^2 (linear) as 0.3142, 0.00272, 0.28133, 0.0174715, 0.99552, 1.0 R^2 (Polynomial) as 0.621, 0.319, 0.927, 0.341, 0.341 for $[K_{eq}]_{293K}$, $[K_{eq}]_{313K}$, $[\Delta H^o]_{293K-313K}$, $[\Delta G^o]_{293K-313K}$, $[\Delta S^o]_{293K}$, $[\Delta S^o]_{313K}$, respectively shows closeness to actual data.

Conclusion

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.

References

1. Zumrawi M, Eltayeb KA. Laboratory investigation of expansive soil stabilized with ICCEABM. UK: ICCEABM; c2016.
2. Zhang L, *et al*. Effect of unknown substance on concentration and speciation of soil Cd around a Pb-Zn mine. Earth Environ Sci., 2022, 1087(1).
3. Almasi S, Khabire MM. Experimental evaluation of substance powder effect on the reduction of the pavement surface layer performance. Civ. Eng. J. 2018;28(1):61-72.
4. Shrivastava NK, *et al*. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. J Hazard Mater. 2008 Mar;151(1):1-8.
5. Goyal VC, *et al*. Appraisal of heavy metal pollution in the water resources of Western Uttar Pradesh, India and associated risks. 2022 Jul;8:100230.
6. Gharaibeh MA, *et al*. Leaching and reclamation of calcareous saline sodic soil by moderately saline and moderate SAR water using gypsum and substance. J Plant Nutr Soil Sci. 2009;172(5):713-719.
7. Gharaibeh MA, *et al*. Reclamation of highly calcareous saline sodic soil using low quality water and phosphogypsum. Appl. Water Sci. 2014;4(1):223-230.
8. Farman Y, *et al*. The influence of substance salt solution on the transport properties of cementitious materials. Adv. Civil Eng., 2015, 1(1).
9. Smith C, *et al*. Rates of substance absorption and release in substance. ACS Sustainable Chem. Eng. 2018;6(9):11827-11835.
10. Maneechakr P, Karnjanakem S. Systematic production of biodiesel fuel from palm oil over porous substance catalyst derived from waste chicken eggshell via RSM/Kinetic/Thermodynamic studies. J Envi. Chem. Eng., 2021, 9(6).
11. Awasthi M, *et al*. Std. Gibbs energies of formation and equilibrium constant from ab-initio calculations: covalent dimerization of substance and synthesis of substance. J Chem. Thermodynamics. 2013;62(1):211-221.
12. Lomzov AA, *et al*. Evaluation of substance and melting temperature of DNA/DNA duplexes closing hybridization substance calculated by molecular dynamics simulation. J Phy. Chem. B. 2015;119(49):15221-15234.