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Original Research Paper

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MATHEMATICAL KINETIC AND THERMODYNAMIC STUDY OF ADSORPTION OF COPPER II BY ALKALINE SOIL USING BATCH METHOD

Neelam Chaudhary Department of Chemistry, Career point University.

Dr. Bhartiy Sharma Associate Professor and Head MBPG, College, Kota.

ABSTRACT Contamination of soil with heavy metal directly depends upon the adsorption capacity of metal either onto the soil or leaching from soil which tends to have long time or instantaneous effects to soil qualities and related cofactors. In this way the aim of this work was to study the adsorption of copper (II) on to the soil in different depth as [SS]0-15 and [SS]15-30. Rate of adsorption of ion from 0 minute to infinite were observed and found nearest to first order reaction after calculation. The calculated values of data gave the gibbs free energy negative which indicates spontaneity of ion adsorption process in soil sample from different depth of selected area.

KEYWORDS :

INTRODUCTION:

With developing technologies a main problem arise of heavy metals pollution(1). Non biodegradable and accumulation nature of copper can lead various diseases and disorders in all the living organisms and human beings and contaminate the soil and water qualities too (2). Accumulation of Cu(II) is significantly toxic to human beings and the ecological environmental (3). With the help of adsorption technique (4) we can find out the various ways to measure the concentration of copper in adsorption capacity (5) and connected way to sort out the problem of contamination of such heavy metals(6). As copper mainly exist in complexed form in two types redox state (7) found in different state through changing in depth of soil (8) and temperature changings (9). In order to understand adsorption efficiency of copper adsorption kinetics, studies were done which describes residential or uptake time of solute on solvent at the solid solution interface. The kinetics parameters can scale up studies of soil remediation process connecting optimum operational conditions of copper (II) predicting by important directional or non-directional operations of the ion adsorption and remidial operations (12, 13). The obtained data was indeed near to first order rate law (14). As temperature can make two types effects on the adsorption process as physical adsorption and chemical adsorption which are opposite qualities in the reference of increasing temperature (15). So only temperature changes is not sufficient parameter to determine the type of adsorption. Thus Gibbs free energy ΔG° was too observed and calculated of each experiment to know whether the reactions are spontaneous or non spontaneous or feasible.

MATERIALS AND METHODS:

From two different depth $[SS]_{0-15}$ and $[SS]_{15-30}$, soil samples were collected, dried and seived to get uniform particle size. The effect of temperature on the adsorption of copper (II) was investigated at different temperature 25° and 35°C for $[SS]_{0-15}$ and $[SS]_{15-30}$, into 250ml of conical flask containing 100 ml of 1 mg copper II solution taken from stock solution of $CuSO_4$ while the soil amount was taken 2gm in 100 ml solution at pH range of 7 to 8. In thermostate conditioned concentration change of copper was noticed with different contact times (2, 4, 6, 8, 10, 12, 14, 16 and 20 min). The kinetics factors as rate constant (*k*) reaction order (*n*), activation energy (*Ea*) can be calculated by the kinetics chemistry formulaes. The reaction order was found fit in first order reaction through rate integration law method. The thermodynamics factor Gibbs free energy to know reaction feasibility or spontaneity was calculated during each experiment from the following equation $\Delta G° = -RT \ln k_e$, were k_e is the thermodynamics equilibrium constant without units, T is the temperature in kelvin and R is the gas constant k_e were calculated by $k_e = \frac{C_{Ad}}{C_s}$ were c_{Ad} and c_s are equilibrium by $k_e = \frac{C_{Ad}}{C_s}$ where copper (II) on the adsorbent and in the solution respectively.

Table A : Variations in Cu(II) with temperature range from 25°C and 35°C on to $[SS]_{15-30}$ with Cu(II) ion in 2gm soil maintain pH 7-8.

Temp °C	25			35		
Time, min.	Unad	Ad	% Ad	Unad	Ad	% Ad
0	0.500	0.000	0.00	0.500	0.000	0.00
2	0.350	0.075	30.00	0.330	0.085	34.00
4	0.320	0.090	36.00	0.290	0.105	42.00
6	0.300	0.100	40.00	0.270	0.115	46.00
8	0.280	0.110	44.00	0.240	0.130	52.00
10	0.250	0.125	50.00	0.200	0.150	60.00
12	0.220	0.140	56.00	0.180	0.160	64.00
14	0.190	0.155	62.00	0.150	0.175	70.00
16	0.160	0.170	68.00	0.140	0.180	72.00
18	0.160	0.170	68.00	0.140	0.180	72.00
20	0.160	0.170	68.00	0.140	0.180	72.00
	0.160	0.170	68.00	0.140	0.180	72.00
	Mean = 47.45454545			Mean = 53.09090909		
	S.D. = 20.76710686			S.D. = 22.09730547		

* $[SS]_{0-15}$ – Soil Sample Depth
* Unad – Unadsorbed amount of Cu (II) mg/gm
* Ad – Adsorbed amount of Cu (II) mg/gm
* % Ad – Percentage Adsorption

Table B : Variations in Cu(II) with temperature range from 25°C and 35°C on to $[SS]_{0-15}$ with Cu(II) ion in 2gm soil maintain pH 7-8.

Temp °C	25			35			
Time, min.	Unad	Ad	% Ad	Unad	Ad	% Ad	Unad
0	0.500	0.000	0.00	0.500	0.000	0.00	0.500
2	0.330	0.085	34.00	0.315	0.093	37.00	0.305
4	0.310	0.095	38.00	0.290	0.105	42.00	0.270
6	0.290	0.105	42.00	0.270	0.115	46.00	0.240
8	0.260	0.120	48.00	0.230	0.135	54.00	0.200
10	0.220	0.140	56.00	0.200	0.150	60.00	0.160
12	0.180	0.160	64.00	0.160	0.170	68.00	0.140
14	0.140	0.180	72.00	0.130	0.185	74.00	0.120
16	0.140	0.180	72.00	0.130	0.185	74.00	0.120
18	0.140	0.180	72.00	0.130	0.185	74.00	0.120
20	0.140	0.180	72.00	0.130	0.185	74.00	0.120
	0.140	0.180	72.00	0.130	0.185	74.00	0.120
	Mean=	51.81818182		Mean=	54.81818182		
	S.D.=	22.58237446		S.D.=	22.88588291		

* $[SS]_{15-30}$ – Soil Sample Depth
* Unad – Unadsorbed amount of Cu (II) mg/gm
* Ad – Adsorbed amount of Cu (II) mg/gm
* % Ad – Percentage Adsorption

Thermodynamic Parameter:

The estimation of standard Gibb's free energy was observed to be more negative with increase in temperature. The negative values indicates feasibility and spontaneous nature of adsorption of a high preference of Cu (II) on to $(SS)_{0\text{-}15}$ &$[SS]_{15\text{-}30}$ from zero minute to infinite times during the temperature of 25°C & 35°C- changes and values of ΔG° are calculated as:-

Temp (°C)	$K_e = c_{Ad}/c_e$	$\ln k_e$	$\Delta G° = -RT \ln k_e$ KJ mol^{-1}
25°	1.063	0.061	–0.153
35°	1.286	0.251	–0.644

for $[SS]_{0\text{–}15}$

Temp (°C)	$K_e = c_{Ad}/c_s$	$\ln k_e$	$\Delta G° = -RT \ln k_e$ KJ mol^{-1}
25°	1.295	0.291	–0.631
35°	1.423	0.353	–0.903

for $[SS]_{15\text{–}30}$

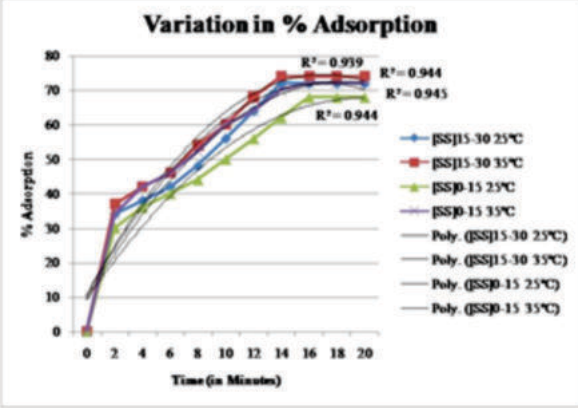

Fig.A Mathematic representation of distribution of % adsorption data of $[SS]_{0\text{-}15}$ and $[SS]_{15\text{-}30}$

RESULT AND DISCUSSION:-

Very interesting result was obtained during entire work process of adsorption of copper II during a temperature range of 25°C and 35°C with contact time in minutes. Adsorption part were calculated against not adsorption part in order to get percentages of adsorption of ion during entire process. Adsorption concentration changes were running according around first order to pesudo second orders reaction. Equilibrium constant were calculated and than further gibb's free energy (ΔG°) was calculated during each experiment. Negative values of gibb's free energy indicate reaction is how much spontaneous and copper II ions adsorption is too much spontaneous process. And with increasing temperature adsorption was too found in increasing order which indicate the adsorption process take place fastly with increasing temperature. With increasing temperature particles potential energy too increases and adsorption process take fastly move. Mathematical modling proves that with going upward to temperature and downward to depth % adsorption increases as mean value increase from 47.46 to 53.10 at $[SS]_{0\text{-}15}$ while 51.82 to 54.82 at $[SS]_{15\text{-}30}$ and standard deviation from 20.77 to 22.10 at $[SS]_{0\text{-}15}$; 22.58 to 22.88 at $[SS]_{15\text{-}30}$. Polynomial regression clarify how adsorption % varies with depth and temperature change in the time duration as $[SS]_{0\text{-}15}$ at 25°C is taken independent variable and $[SS]_{15\text{-}30}$ dependent variables are modelled against the 35° & 45° degree polynomial in $[SS]_{0\text{-}15}$ by giving the closest data to real data as R^2 from 0.939 to 0.945.

CONCLUSION-

The entire process of thermodynamics 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 capacities of heavy metals in the soil and these contamination boundaries.

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