Adsorption Studies of Leucine and Glutamic Acid on Montmorillonite Clay in Presence and Absence of Cu^{2+}, Ca^{2+} and Mg^{2+} Metal Ions in Relevance to chemical Evolution

Kavita Gururani and Chandra Kala Pant
Department of Chemistry, D.S.B. Cmapus, Kumaun University Nainital (Uttarakhand), India- 263001.

Abstract:-In the present work, surface interaction of leucine and glutamic acid gas been investigated on Montmorillonite clay, or without metal ions (Cu^{2+}, Ca^{2+}, Mg^{2+})as a function of pH (3.6-5.5 and 6.8-9.2), temperature (25^0-35^0C) and concentration ($7.0X10^{-5}$M-$2.0X10^{-5}$M). Adsorption parameters (Xm and K_L) calculated from Langmuir adsorption isotherms. It was observed that adsorption trend (% binding, values of Langmuir constants) of adsorbate adsorbed on montmorillonite clay (M) with or without cations largely depends on the nature of adsorbate as well as adsorbent.

Keywords: -Montmorillonite, Chemical Evolution, Surface interaction, Langmuir isotherm.

Introduction: -**Bernal**[1] suggested that clays might have played a significant role in primitive earth through the processes of concentration and adsorption of the biologically formed biomonomers and thus protecting then against the hydrolytic fission. During the activity of various radiations, large number of biomonomers formed have been trapped by clays, silica and alumina through adsorption and condensation[2].

Rao et. al[3] **and Ponnamperuma et. al**[4]. have reviewed the possible role of clay minerals in the process leading to the origin of life and strengthened Bernal's hypothesis.

Kamaluddin et. al[5] have reported the adsorption of amino acids on transition metal ferrocyanides as possible adsorbents in primitive lifeless era. **Ferris and coworkers**[6], **Lahav et. al**[7]. Have reported that clay minerals as insoluble alumina silicates exhibit high adsorption capabilities in the process of amino acid.

Recently **Budjak and Coworkers**[8], **Basuik et.al.**[9], **Yanagawa and Kobayashi**[10] have suggested that clays and silicon might have catalysed oligomerisation reactions of amino acids leading to the evolution of proteins.

Experiment concerning adsorption of amino acids have been carried out reviewed **(Kalra et. al. 2000**[11], **Meng et. al. 2004**[12], **Zaia 2004**[13], **Whitehouse et.al. 2005**[14], **Kuwamara et. al. 2009**[15], **Pant et.al. 2009**[16], **Pandey et.al. 2013**[17] , **Pandey et. al. 2015** [18]**).**

Experiments carried out in our laboratory have shown that the adsorption isotherm were dependent on the nature of the adsorbate, adsorbent and pH of the suspension

Experimental:-

All the reagents were of analytical grade. Montmorillonite clay was purchased from Aldrich Chemical Co. Adsorption studies of leucine and glutamic acid were studied on montmorillonite clay and cation exchanged clay in triple distilled water. The concentration of the reaction solution after adsorption were recorded by using Jasco- V-550 UV spectrometer and pH was measured in a digital pH meter. Montmorillonite was repeatedly washed with distilled water and dried at 25^0C before use, portion of clay (50mg) were used in each investigation.

Firstly, adsorption of leucine and glutamic acid was studied as a function of pH and concentration of adsorbate. Therefore, adsorption of these adsorbate in varying concentration ($7X10^{-5}X2X10^{-5}$) on montmorillonite and cation exchanged clay (50mg) over a wide range of pH between 3.0-9.2 was studied by adding appropriate buffer to 5 ml. solution of adsorbate. Acetate buffer (0.2N acetic acid and 0.2N sodium acetate) and borax buffer (0.2M boric acid and 0.05M borax) were used to maintain pH in the range 3.6-5.5 and 6.8-9.2 respectively.

Buffered solution of adsorbate (5 ml each) was added to montmorillonite clay and cation exchanged clay (50mg) placed in separate ground flask (50 ml). The flasks were capped and the content were stirred mechanically for 20 minutes and allowed to stand at room temperature for 8 hrs. Similar sets of amino acids were incubated at different temperatures and pH to find out the condition of maximum adsorption. After 8 hrs, the experimental solution containing different adsorbents were centrifuged at 3000 rpm for 15 minutes.

The concentration of all adsorbates used, in the supernatant were determined using Jasco – V- series UV spectrophotometer at wave length of maximum adsorption of respective adsorbate. The amount of adsorbed amino acids (leucine, glutamic acid) were calculated by the difference between the concentration of respective adsorbate before and after adsorption. The equilibrium concentration of adsorbates and the amount adsorbed were used to obtain the adsorption isotherm.

The concentration of glutamic acid and leucine in the supernatant were determined by recording their absorbances at λ max 198.5 nm and 196.5 nm respectively.

The values are summarized in table 1 and illustrated in figures A(a,b,c) and B(a,b,c).

Results and Discussion:-

The surface interaction of amino acids on montmorillonite clay with or without divalent cations (Cu^{2+}, Ca^{2+}, Mg^{2+}) was studied as a function of time, pH and concentration.

From the figures it appears that the amount of amino acids adsorbed increases as their equilibrium concentration increases in solution up to a certain limit i.e. saturation point. Above this point adsorption becomes independent of the concentration. Initially, the curve shows linear relationship between amount adsorbed and equilibrium concentration, whereas at higher concentration, saturation point occurs and no adsorption takes place. The asymptotic nature of adsorption isotherm (Fig A and B) suggested Langmuir type adsorption or monolayer formation as given below:-

$$\frac{Ceq}{Xe} = \frac{1}{K_{L}\,Xm} + \frac{Ceq}{Xm}$$

Where,

Ceq = Equilibrium conc. of amino acids

K_L = Constant related to energy i.e. enthalpy of adsorption coefficient

Xe = Amount of adsorbate (mg) adsorbed per gm of adsorbent

Xm = Amount of adsorbate required for a weight of adsorbent for forming a complete monolayer on the surface.

The adsorption parameters Xm and K_L were calculated from the slope and the intercept obtained from the graph of Ceq/Xe versus Ceq. Values are summarized in table 1.

The value of Xe can be calculated asymptotically from figs A and B on extrapolating the adsorption curve towards Y- axis when saturation phenomenon occurs. It was observed that adsorption trend of adsorbate adsorbed on montmonillorite clay with or without cations largely depend on the nature of adsorbate as well as adsorbent.

Results of adsorption of glutamic acid and leucine are recorded in table I. in terms of percent binding. Percent binding has been calculated with the help of optical densities of respective biomonomer solution before and after adsorption corresponding to saturation points on the curves.

The percent binding of glutamic acid and leucine appear to have the following order:

Leucine > Glutamic acid

The effectiveness of various adsorbents towards the adsorption of glutamic acid was as follows:

M- Mg^{2+}>M-Cu^{2+}>M-Ca^{2+}>M

Whereas, for leucine the order was as follows:

M- Cu^{2+}>M-Mg^{2+}>M-Ca^{2+}>M

Thus, addition of Mg^{2+}, Cu^{2+},Ca^{2+} increases the adsorption throughout the entire range of concentration. This shows that the increase in ionic strength of clay, increase the attractive force between the amino acid and clay surface. Based on the observations, the main role of inorganic cations in the adsorption of amino acid on clay may be accounted as the neutralization of divalent cations in between.

The Xm values recorded in Table 1 revealed that the effect of metal cations incorporated clay on adsorption of glutamic acid was relatively more significant than leucine. The divalent metal cation act as a bridge in between the two negative charges and thus due to higher electrostatic forces of attraction, the complex become stable in the aqueous environment of primitive sand beds, sea or sea shore. In some cases, the K_L value, which is characteristic of measure of energy associated during adsorption show the intercept and thus the adsorption process is facilitated with the release of energy i.e. exothermic reaction.

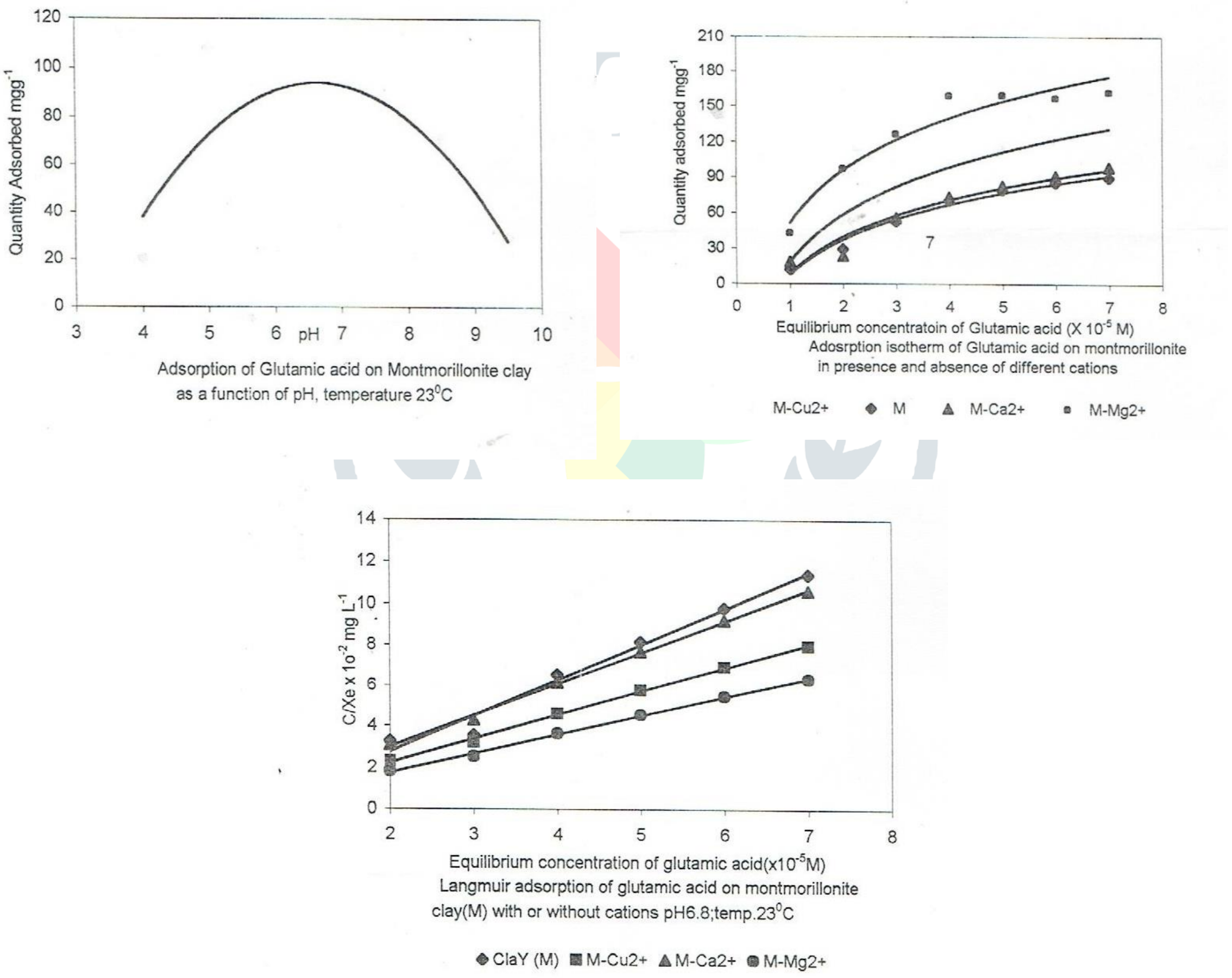

Figure : A (a,b,c)

Table 1

Percent binding and Langmuir constants for adsorption of glutamic acid and leucine on Montmorillonite Clay (M) with or without different cations

Percent binding (%)			Langmuir Constants			
Type of adsorbent	**Glutamic Acid**	**Leucine**	**Glutamic Acid**		**Leucine**	
			X_m (mgg^{-1})	K_L (Lmg^{-1})	X_m (mgg^{-1})	K_L (Lmg^{-1})
Montmorillonite Clay (M)	52.73	60.10	90	-2.0075	120	-119.9
M-Ca^{2+}	53.25	61.50	96	24.33	110	112.07
M-Cu^{2+}	54.45	64.30	128	26.46	116	-89.31
M-Mg^{2+}	60.28	62.10	162	33.17	112	-86.25

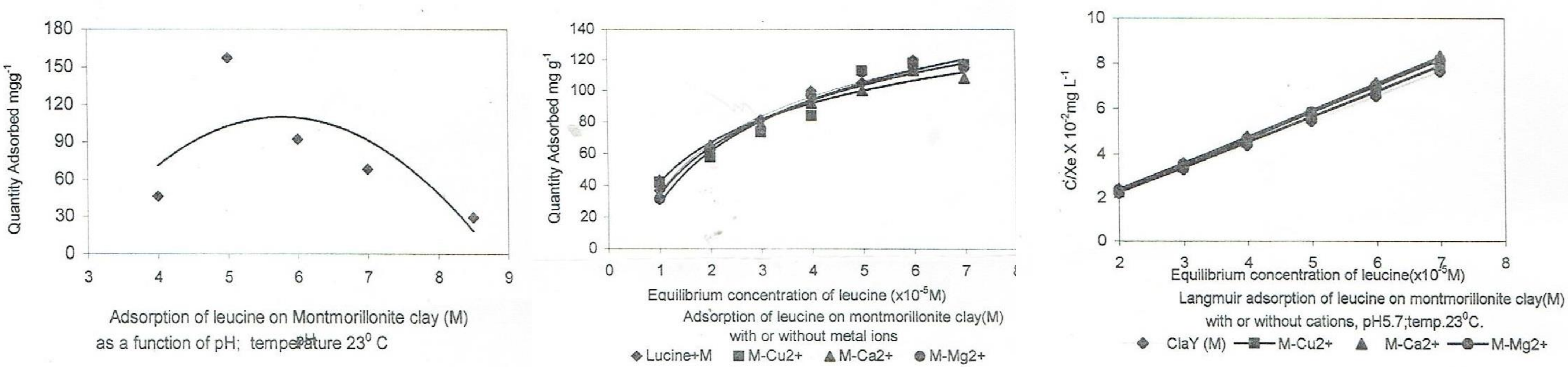

Figure B (a, b, c)

References

1. Bernal, J.D.: : 1951, the Physical Basis of life, Rationalist Annual, 148, 3-10
2. Paecht-Horowitz; M.Berger and Katchalsky, A. : 1970, Nature. 228, 637.
3. Rao, M; Odom, D.G. and Oro,J. : 1980, J Mol. Evol, 15, 317
4. Ponnamperuma,C.; Lemmon, R.M; Mariner, R. and Calvin,M. : 1963, Proc. Natl. Acad. Sci. U.S.A. 49, 737
5. Kamalludin, Nath, M. and Sharma, A. : (1994) Origins of life and evolution of biosphere, 2, 469-477.
6. Ferris, J.P.;Zamek, O.S. Altbuch, A.M. and Frieman, H. : (1974 b) J. Mol. Evol. 3, 301-309.
7. Lahav, N.; White, D. and Chang : 1978, Science, 201, 67-69.
8. Rode, B.M., Son, H.L, Suwanochat, Y. Bujdak, J. : 1999, The combination of salt induced peptide formation and reaction and clay catalysis, A way to higher peptides under Primitive earth conditions. Origins life Evol. Biosphere 29, 273-286.
9. Basiuk, V.A. and Sainz Rojas, J. : 2001, Catalysis of peptide formation by inorganic oxides. High efficiency of alumina under mild conditions on the earth-like planets. Adv. Space. Res, 27, 225-230.
10 Yanagawa, H and Kobayashi,K. : 1985, J. Biochem, 97, 1521.
11. S. Kalra; C.K. Pant; H.D. Pathak; M.S. Meheta. : 2000, Ind. J. Biochem, Biophys, 37, 341-346.
12. Ming Meng, Lorenzo Steivano, and Jean- Francois Lambert : 2004, Adsorption and thermal condensation mechanism of amino acids on oxide. Glycine on silica. Langmuir 20; 914-923.
13. Zaia, D.A.M. : 2004, A review of adsorption of amino acids on minerals; was it important for origin of life? Amino acids 27, 113-18.
14. White, D.H. and Erickson, J.C. : 1980, J. Mol. Evol. 17-19.
15. Kunio Kuwamura; Hitoshi Takeya; Tokao Kushibe. : 2009, Effect of condensation agents and minerals for oligopeptide formation under mild and hydrothermal conditions related to chemical evolution of proteins. Advances in space research, 44, 267-275.
16. Pant, C.K.; Hemlata, Pathak, H.D. : 2009, Heat initiated prebiotic formation of peptides from glycine/ aspartic acid and Glycine/ valine in aqueous environment and clay suspension. International Journal of Astrobiology 8(2); 107-115.
17. Pramod Pandey; C.K. Pant; Kavita Gururani et. al. : 2013, Surface inter- action of L- alanine on Hematite; An Astrobiological implication Orig. Life Evol Biosph (2013) 43; 331-339.
18 Pramod Pandey; C.K. Pant; Kavita Gururani et. al. : 2015 Affinity of Smectite and Divalent Metal Ions (Mg^{2+} Ca^{2+} Cu^{2+}) with L- leucine. An Experimental and theoretical Approach Relevant to Astrobiology. Origins of life and Evolution of Biospheres. DOI 10.1007/s 11084-015-9437-2.

Acknowledgement: - The author is thankful to the Head, Department of Chemistry for providing necessary research facilities.