

International Journal of Scientific Research and Reviews

Adsorption of L-Aspartic Acid onto Montmorillonite Clay and Cations Exchanged Montmorillonite Clays

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ABSTRACT

Adsorption of L-aspartic acid was consistently studied on the surface of eco-friendly montmorillonite and cations (Ca^{2+} , Mg^{2+} and Ni^{2+}) exchanged mClays. Adsorption studies have been done in aqueous media as a function of pH (9.2 - 3.0) in the concentration range of ($9.0 \times 10^{-5}\text{M}$ - $1.0 \times 10^{-5}\text{M}$) and temperature of (20 - 25°C). The process of adsorption was supervised consistently by measuring the absorbance of L-aspartic acid solution at a wavelength (λ_{max}) 205 nm. The amino acid binding percent (%) is calculated in terms of its absorbance. The maximum amount of L-aspartic acid was adsorbed at neutral pH (7.0 ± 0.01) and a temperature of 25°C. A Langmuir type of adsorption isotherm was intended for the various concentration ranges of the experiments. It was agreed that calcium-exchanged montmorillonite was a superior L-aspartic acid adsorbent in all cases studied. The adsorption parameters, i.e., K_L and X_m have been calculated using L-isotherms as the plot is linear with a correlation coefficient (r^2) of 0.9. A thermodynamic benign exothermic reaction is observed, based on the values of Gibbs free energy (G^0).

KEYWORDS

Adsorption, L-aspartic acid, Amino acid (AA) Montmorillonite clay (mClay), Cation- exchanged clays

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INTRODUCTION

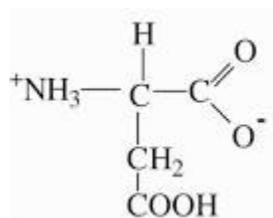
Clay minerals are the beneficial materials available in nature with an increasing understanding of clay structure. Montmorillonite and other clay minerals are recognized as a viable material for improved performance in a variety of materials and products such as catalysis, food additives, antibacterial function, polymer sorbent, and beauty products, among others¹⁻⁴. As it has been served by the researchers^{5,6} that montmorillonite is a very delicate disilicate group of minerals from when they precipitate from water and a member of the smectite family, is a 2:1 clay substitute, having two tetrahedral sheets of silica sandwiching a central octahedral sheet of alumina⁷⁻⁹. The main benefaction to the surface charge of montmorillonite layers is the stable negative charge on the basal planes due to isomorphic substitutions¹⁰. Several experiments^{11,12} have been carried out to synthesize peptides from amino acids catalysed by clay minerals such as montmorillonite, kaolinite hectorite, bentonite etc. Peach – Horowitch¹³ announced that montmorillonite catalyses peptide bond formation from an aqueous medium of an activated amino acid adenylate. Our work¹⁴ on L-valine on mClay and cation exchanged mClay studies have shown that it ideally adsorbs anions, forming surface bonds through the two carboxylate oxygen atoms and the nitrogen atom of the amino group. In addition, there is a strong proclivity to form hydrogen bonds with other molecules on the surface, which in some cases, leads to the loss of surface coordination and for the formation of dipolar species. The successful work of L-valine¹⁴ aimed to explore the work with another amino acid which is acidic in nature and one of the most plentiful AA L-aspartic acid ($\text{HOOC.CH}(\text{NH}_2)\text{CH}_2\text{COOH}$) in nature, and it has three functional groups: alpha-amino group, an alpha-carboxyl group and beta-carboxyl group which can interact with the metal surfaces their role of surface interaction with mClays and their cation exchanged properties in the uses of pre-biotic formation of bio-molecules. As we know bio-molecules are available on earth's crust in different conformations. Amino acids are the most important component of life on Earth because they are the building bricks of proteins, enzymes, and muscle tissue, all of which are required by all living things for proper body functioning and allied anatomical processes.

MATERIALS AND METHODS

Calcium (II) chloride, magnesium (II) chloride, and nickel (II) chloride were achieved by BDH Company USA. All the chemicals were of analytical grade and used without further purification. Solutions were developed in triply deionized water. X-ray diffraction measurements were performed on $<2\ \mu\text{m}$ samples. Calcium, magnesium, and nickel Homo-ionic clays were prepared by saturation method¹⁵ with 50ml of the 1M concentration of each metal chlorides. The excess of the salts was percolated out by washing and centrifugation procedures were separated until the chloride ion was no longer detected by silver nitrate¹⁶. Finally, divalent cation exchanged forms thus acquired were dried under a vacuum at room temperature. The dried product was unagitated and sieved to a particle size of $125\mu\text{m}$. The adsorption of AA i.e., amino acid on mClay and cation exchanged mClays in an aqueous medium was studied as a function of pH, temperature, and concentration of adsorbate. To obtain saturation point by adding an appropriate buffer to the AA containing montmorillonite/Ca/Mg/Ni incorporated montmorillonite keeping in mind, that the buffer should be a very weak ligand so that suitable complex formation with clay could be avoided. Buffers used were 0.2M KCl and 0.2M HCl for pH 1.0–2.0, 0.2 M CH_3COOH and 0.2M CH_3COONa for pH 3.0 - 8.0, 0.2M borax and 0.2M HCl for

pH 9.0 and 0.2M borax and 0.2 M NaOH for pH 10.0. The pH of the solution was verified using an Agronic digital-511 pH meter. This was also verified by conductivity measurement, as there is no change in the inflection point by titration buffer against the salt solution. A buffered 10ml AA solution was added to conical flasks containing 50mg of mClay and cation exchanged mClays and mechanically stirred for 15 minutes before being left at room temperature for 18 hours. Similar sets of varying concentrations of AA with various adsorbents were incubated over a temperature range of 20-25⁰C for varying periods and pH to find out the conditions of maximum adsorption. After about 18 hrs of maturation, the suspension was centrifuged in Teflon-coated tubes at 3500rpm for 30min. The supernatant was decanted and the AA concentration of L-aspartic acid was measured spectrophotometrically at 205 nm at neutral pH7.0. Before the start of the experiment, the laboratory glass vessels were sterilised at 160⁰C for 30 min and then covered with aluminium foil (bacteria in the air can eat AA). The amount of AA adsorbed was calculated based on the difference in concentrations before and after the adsorption of each experiment. It was observed that additional maturation time did not appreciably change the degree of adsorption. The absorbance of L-aspartic acid (pKa_{COOH}=2.3, pKb_{NH3}=9.6) was measured spectrophotometrically at corresponding λ_{max} 205nm. The equilibrium concentration and the amount adsorbed were used to obtain the adsorption isotherm (Indirect method). In the direct method, absorption spectra were documented using the Jasco-V550 Spectrophotometer to attain the quantity of AA adsorbed on clays which were further verified by the desorption of AA from their clay complexes formed after equilibrium and frequently washed by resuspending the centrifuged pellets in 1ml of double distilled water until no more amino acid was detected in the suspension (spot test colour with ninhydrin reagent at 570 nm) and then the optical density was measured ¹⁷.

RESULT AND DISCUSSION

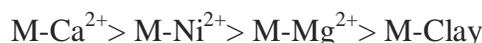


To achieve maximum adsorption, the adsorption of L-aspartic acid (structure, above) on mClay and cation-exchanged clays in an aqueous medium was studied at pH 3.0-9.2, temperature range of 20-25⁰C, and a concentration range of 9.0 x 10⁻⁵M-1.0 x 10⁻⁵M of the adsorbate. Moreover, the main purpose is to study the adsorption of L-aspartic acid on mClay with or without divalent cations as an adsorbent for preferential adsorption under pre-biotic conditions believed to have existed near the lithosphere-hydrosphere boundary of the primitive sea or on the bottom of the sea. The study of adsorption as a function of temperature showed maximum adsorption at 25⁰C. Elementary studies have shown that the amount of L-aspartic acid adsorbed on mClay is pH-dependent, with a maximum at pH 7.0. In all case studies involving L-aspartic acid adsorption, subsequent investigations were carried out at pH 7.0 and a temperature 25⁰C (the constant temperature was maintained by an ultrathermostate). The effects of pH on the adsorption of L-aspartic acid on mClay at a temperature at 25⁰C are shown in Fig.1 and the results are noted in Table1

Adsorption studies of L-aspartic acid as a function of pH specified that initially up to pH7.0 the adsorption was increased and decreased after that, as shown in Fig.1, this trend appears in all cases studied of L-aspartic acid. Therefore, neutral pH was chosen to run the maximum adsorption of L-aspartic acid in a broad concentration range because the neutral pH is anatomically notable and most of the oxidoreduction reactions in biological systems take place in a neutral medium. Though, the inherent dipolar nature of amino acids also furnishes some insight into the pH effects. Under acidic conditions, amino acids occur as cations however as the pH of the solution tends towards neutrality, the dipolar form exists. I noticed that L-aspartic acid has an isoelectronic point value of 6.0. The more substantial adsorption of AA was observed at pH above the isoelectric point (>6.0) indicating that the adsorption occurs in the form of anions¹⁸. The higher adsorption of L-aspartic acid on clay and cation-exchanged could be due to interactions of AA with replaceable divalent cations: Ca (II), Mg (II) and Ni (II) present in the clays. At higher pH (>7.0) appreciable decrease in adsorption of L-aspartic acid on mClay with or without cation exchanged mClay was observed. This may be because at higher pH, coordination of available hydroxide with divalent cations becomes ambitious with that of adsorbates. Effects of pH on the adsorption of L-aspartic acid studies showed that L-aspartic acid is adsorbed in an anionic form on adsorbents. It may be due to the presence of the amino group and a carboxylic group which appears as a site for interaction with the clay surface. The percent (%) binding shown in fig. 2 was calculated with

$$\% \text{ Binding} = (C_{BF} - C_{AF})/C_{BF} \times 100$$

C_{BF} and C_{AF} are concentrated after adsorption, respectively. The value of maximum uptake of L-valine was observed on montmorillonite and cation exchanged clays are in the following trend:



The adsorption isotherms C_{eq} (equilibrium adsorbate concentration) as a function of concentration, i.e., the adsorption of L-aspartic acid on clay with or without cation exchanged clays exhibit a linear relationship. Adsorption increases rapidly at lower amino acid concentrations. The adsorption increases rapidly. However, at higher concentrations, saturation appears to render more adsorption. The asymptotic nature of the adsorption isotherm was shown in Fig. 3 and indicated the Langmuir type of adsorption or monolayer formation. Langmuir plots exhibit the amount of AA (L-aspartic acid) adsorbed as a function of their equilibrium concentration. The adsorption of AA on adsorbents follows the Langmuir equation¹⁹

$$\frac{C_{eq}}{X_e} = \frac{C_{eq}}{X_m} + \frac{1}{K_L X_m}$$

Where, C_{eq} is the equilibrium concentration of the AA in solution, X_e in mg the amount of solute adsorbed per gram weight of adsorbent and X_m in mg the amount of solute required per gram weight of adsorbent for complete monolayer formation. K_L a constant related to enthalpy (ΔH) of adsorption ($K_L \propto e^{-\Delta H/RT}$) the parameter K_L reflects the steepness of the approach to saturation, more precisely; the K_L value is the reciprocal of concentration at which half of the saturation of the adsorbent is attained. “ K_L ” is a constant, which is a function of adsorption energy.

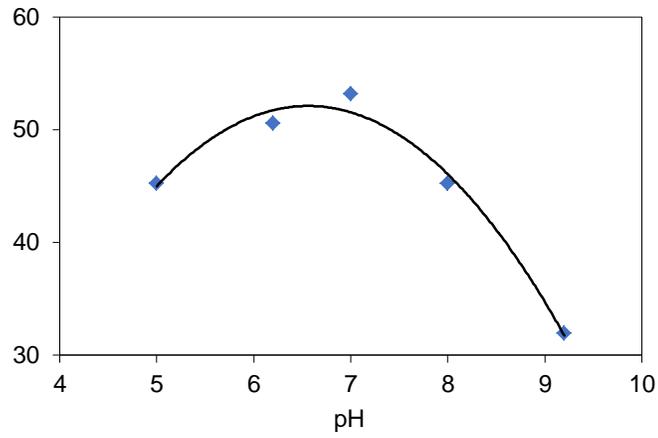


Fig. 1. Adsorption of L- aspartic acid on mClay as a function of pH; temperature 25⁰C

Table 01 L-aspartic acid adsorption on mClays: percent binding and Langmuir constants with or without cations at a temperature of 25⁰C

L-aspartic acid (Ip=6.0)	Adsorbents	%Binding	X _m (m _{gg} ⁻¹)	K _L (l _{mgg} ⁻¹)	r ² (L)
	M-Clay	21.11	50.56	-209.50	0.99
	M-Ca	25.55	61.30	158.71	0.99
	M-Mg	23.33	55.92	214.59	0.99
	M-Ni	24.44	58.94	52.19	0.99

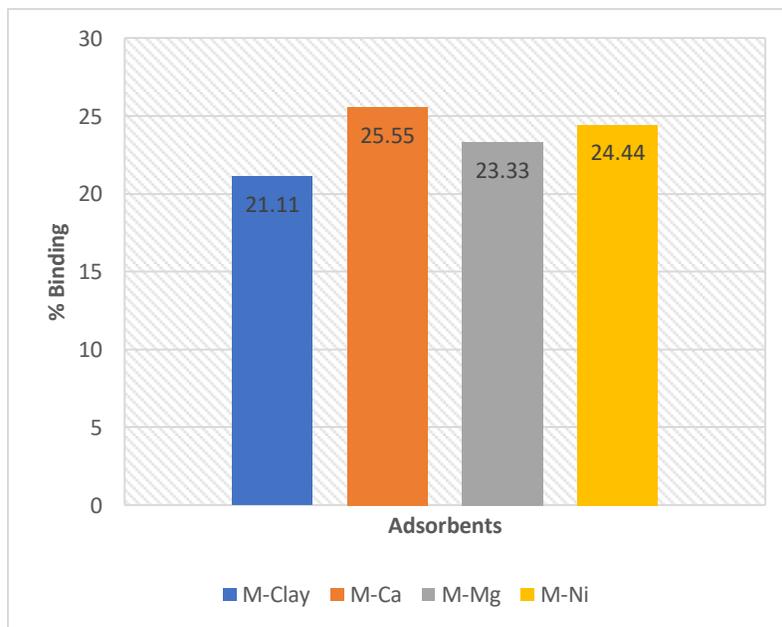


Fig. 2. Percent binding of L-asp acid on mClay and cation exchanged clay surfaces

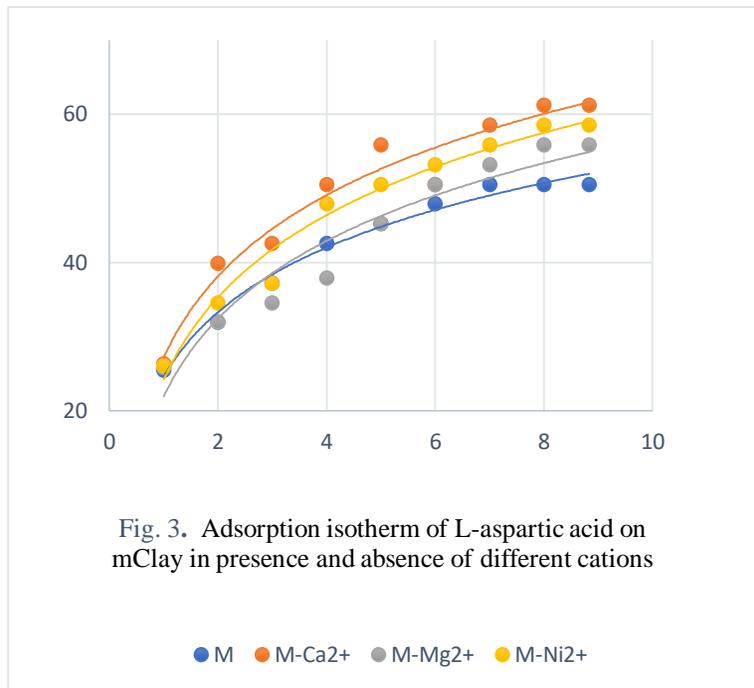


Fig. 3. Adsorption isotherm of L-aspartic acid on mClay in presence and absence of different cations

The pertinent Langmuir adsorption parameters X_m and K_L were calculated from the slope and the intercept was obtained from the graph of C_{eq}/X_e versus C_{eq} . X_e can be calculated asymptotically from Fig.4 on extrapolating the adsorption curve towards Y-axis when the saturation phenomenon occurs. It was noticed that the adsorption mode (% binding and Langmuir constants) of adsorbate adsorbed on mClay with or without cations largely commits on the nature of the adsorbate as well as an adsorbent.

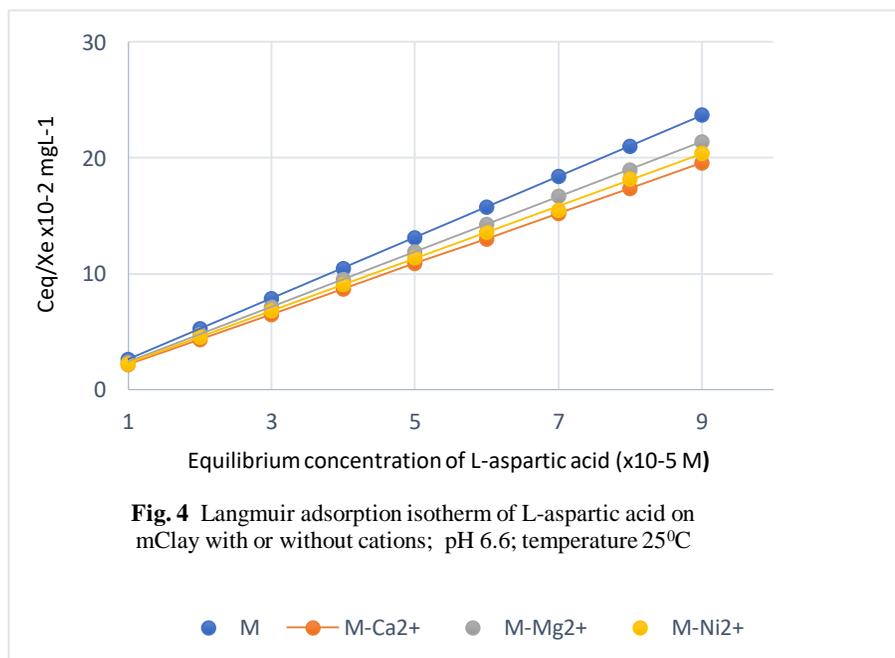


Fig. 4 Langmuir adsorption isotherm of L-aspartic acid on mClay with or without cations; pH 6.6; temperature 25°C

Results and facts were further supported by the thermodynamic free energy (ΔG^0) considerations, calculated, by the following equations^{17, 20}.

$$\Delta G^0 = -RT \ln K^0 \dots\dots\dots (i)$$

$$\ln \frac{K_{T2}}{K_{T1}} = \frac{-\Delta H^0}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \dots\dots\dots (ii)$$

Where K_0 is the thermodynamic equilibrium constant determined by plotting the slope of linear Langmuir adsorption curves. C_{eq}/X_e and equilibrium concentration in the Y-axis C_{eq} in X-axis R is the gas constant, and T is the absolute temperature. With the equilibrium constant K_0 the changes in standard Gibbs free energy (ΔG^0) of adsorption of L-aspartic acid were calculated in the range of -1.21 to -1.69 kJ mol^{-1} at 25°C. The negative values of ΔG^0 for the adsorption of AA on mClay with or without

cations (Ca^{2+} , Mg^{2+} , Ni^{2+}) indicated a thermodynamically supportive exothermic reaction. All the calculated values are recorded in Table 02.

Table 02 Adsorption of L-asp acid on mClay with or without divalent cations at 25⁰C

L-aspartic acid (Ip=6.0)	Adsorbents	lnK ₀	ΔG ⁰ (kJmol ⁻¹)
	M-Clay	1.98	-1.69
	M-Ca	1.63	-1.21
	M-Mg	1.79	-1.44
	M-Ni	1.69	-1.31

CONCLUSIONS

The adsorption of L-aspartic acid on mClay with or without metal cations substitution is maximum at neutral pH and 25⁰C, these values are of physiological importance as they also correspond to the ideal conditions for various bio-chemical reactions in living systems. The adsorption of L-aspartic acid on all four forms, including mClay follows Langmuir type adsorption, which indicates monolayer formation of adsorbate on the clay surface. The percent (%) binding and X_m values in Table 01 demonstrated that the effect of metal cation assimilated clays was comparatively more significant for adsorbate adsorption. Results reported in this transmission reveal that Ca²⁺-exchanged mClays have better adsorption properties as compared to Ni²⁺, Mg²⁺, and mClay without cations. The thermodynamic studies of mClay - AA complexes have shown that the equilibrium constant K₀, the changes in negative values of standard Gibbs free energy (ΔG⁰) of adsorption of L-aspartic acid as mClay in the presence and absence of different cations, thermodynamically supportive exothermic reactions in the forward direction. In a primeval sea experiencing an oscillating environment mClay and cation exchanged mClays could have behaved as an active surface for concentrating bio-molecules. On the basis of investigations, the role of inorganic cations in the adsorption of amino acids on clay may be assumed as the neutralization of the negatively charged surface of alumino-silicate by intercalation. Further investigations into the adsorption of L-aspartic acid, nucleobases, and sugars on mClays with or without divalent cations may be conducted based on the above. Thus, our study suggests the plausible importance of mineral clays in the selection, concentration and condensation of important bio-molecules during the evolution of the chemical the pre-biotic earth. This procedure could conceivably aid in the formation of polymers in oscillating drying- wetting environments.

ACKNOWLEDGEMENT

Author is grateful to Dr. M. S. Mehata, Department of Applied Physics, Delhi Technological University, Delhi for providing me facilities and valuable suggestions also.

REFERENCES

1. G. Nagendrappa "Organic synthesis using Clay Catalysts, Clays for 'Green Chemistry,'" Resonance, 2000; 64-77.
2. M. R. Dintzner. K. M. Morse, McClelland, "Investigation of the Montmorillonite Clay-Catalyzed [1,3] Shift Reaction of 3-Methyl-2-Butenyl Phenyl Ether," *Tetrahedron Lett.in press*, 2003.

3. Navjeet Kaur and D. Kishore, Journal of Chemical and Pharmaceutical Research, 2012; 4(2); 991-1015.
 4. N. Kitadai, K. Nishiuchi and W. Takahagi, Minerals, 2021;11:234, <https://doi.org/10.3390/min11030234>
 5. N. Lahav and S. Chang, J. Mol. Evol. 1978; 13:57.
 6. Z. Kalpyta; T. Fujita; N. Lyi, Appl. Clay Sci., 2001;19: 5.
 7. R. E. Grim, Clay Mineralogy, McGraw-Hill, New York, 1953.
 8. T. Shichi, K. Takagi, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 2000; 1: 113–130.
 9. E. G. Ralph, Clay Minerology, 2nd edition, McGraw-Hill, New-York, 1968; 39-41.
 10. Van Olphen, An Introduction to clay colloid chemistry, New York and London (Wiley), 1963; 301.
 11. J. Bujdak, A. Eder, Y. K. Yanagai, Simkovicova and B. M. Rode, Origins of Life & Evolution of Biosphere, 1995;25, 431-441.
 12. C. K. Pant, Hemlata, H. D. Pathak, M. S. Mehata, International Journal of Astrobiology, 2009; 8: 107.
 13. M. Paecht-Harowitz, J. Berger, and A. Katachalsky, Nature, 1970; 228: 636.
 14. Hemlata Bhatt, Namrata Pandey and Chandra Kala Pant, Vol 8, Issue 3, International Journal of Innovative Research in Technology 2021; 8(3).
 15. R. D. Harter, and G. Stotzky, Formation of clay-protein complexes, Soil science, Am. Proc., 1971; 35: 383-89.
 16. E. D. Theng, Chemistry of clay organic reactions, Hilger, Bristol. 1974.
 17. S. Kalra, C. K. Pant, H. D. Pathak and M. S. Mehata, Colloids and Surfaces A: Physicochem. Eng. Aspects 2003; 212: 43-50.
 18. B. B. Tewari and N. Hamid, Colloids and Surfaces A: Physicochem. Eng. Aspects. 2007; 296: 264-269.
 19. I. Langmuir, J. Am. Chem. Soc. 1918; 40(1)361.
 20. Y. H. Kim, T. M. Heinze, S. J. Kim and C. E. Cerniglia, J. Environ. Qual. 2004; 33: 257-264.
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