Adsorption Of Adenine (Nucleic Acid Bases) On Metal Ferrocyanides In Relevance To Origin Of Life

Namrata Pandey, Hemlata Bhatt, C.K.Pant, A.M.Painuly, Rakesh Raturi

Abstract: Clay might have played a significant role in primitive earth through the process of concentration and adsorption of the biologically formed biomonomers and thus protecting them against hydrolytic fission. Adsorption of adenine was studied in presence of metal ferrocyananides. Studies carried out have shown that adsorption of adenine was dependent on pH and shows Langmuir adsorption isotherm. Percent binding and values of Langmuir adsorption isotherm on metal ferrocyanides show that adsorption trend largely depend on the nature of adsorbate and the adsorbent.

Keywords: Adsorption, biomonomers, metal ferrocyanides, adsorbate and adsorbent

1. INTRODUCTION:
Life is considered as a complex collection of biomolecules capable of self organising and self replicating. It is now widely accepted that processes of abiogenesis of purines, pyrimidines, sugars and amino acids were intimately linked with the formation of earth crust its hydrosphere and atmosphere as well as nature of energy sources. Bernal [1] had laid the idea of possible role of clay minerals in prebiotic formation of peptides and polynucleotide on primitive earth and suggested that clay minerals may have provided surfaces on to which small biologically important molecules have concentrated and subsequently polymerised. Kobayashi and Ponamperuma[2] proposed that there exist a correlation between the concentration of chemical elements in the primordial sea and their biological behaviour. The availability and relevance of soluble mineral salts in primordial environment has been proposed by Lahav and Chang[3] Ferris,et al[4] and Rode, B.M. et al [5]. Arrhenius[6] also proposed the existence of hexacyanoferrate (II), ferrate(III) on the primitive earth. Kamaluddin et al.[7] have reported the divalent metal cyanides as possible minerals on the primitive earth which have acted as efficient surface providing catalyst for the concentration of amino acids through adsorption. Kamaluddin[7] has reported the adsorption of amino acids and nucleotides on transition metal ferrocyanides as possible adsorbents in primitive lifeless era. The clay minerals as insoluble aluminio silicates exhibit high adsorption and catalytic capabilities, in the process of amino acid and nucleotide polymerized have been reported by workers[3,4]

Insoluble metal ferrocyanide could have produced on the primitive earth due to interaction of cyanides with readily available metal ions in the environment . The insoluble cyanometal complexes could have settled at the bottom of the sea or sea shores and might have catalysed a number of reactions like condensation- oligomerisation and interaction reactions on their surfaces Kamaluddin et al[8] and Ali et al[9]. have reported the adsorption of amino acids and nucleotides on transition metal ferrocyanides as possible adsorbents in primitive lifeless era. Recently Tewari et al[10] studied the adsorption of glycine and β-alanine on metal ferrocyanides. However a comparative study on the adsorption of amino acids of different nature (acidic, basic and neutral) as adsorbate on transition metal ferrocyanides as adsorbents has not been carried out so far. Keeping in view the experiments concerning adsorption of amino acids and their peptides on solid surfaces under prebiotic conditions have been carried out and reviewed by some workers [11-16].

2. EXPERIMENTAL:

2.1. Chemicals:
All the studied were carried out in aqueous medium. So it is necessary to sterilizes the reaction vessels, heated solutions and other apparatus were , therefore sterilized at 25lbs/square inch steam pressure for 30 minutes prior to their use in experiments. The stock solution of adenine (7x10-3M) was prepared in deionised water obtained after triple distillation in an all glass assembly. The concentration of all adsorbates used , in the supernatant were determined using JASCO- V550 UV spectrometer at wavelength of maximum adsorption of respective adsobate.

2.2. Preparation of metal ferrocyanides(Ni, Zn, Mn,Co,Cu)
All the metal ferrocyanides were prepared by Kourims [17] method. Potassium ferrocyanide solution (167ml,0.1 m) was slowly added to solution of respective metal salt(500 ml, 0.1m) with constant stirring. To improve the process of coagulation an excess of metal salt was used . The reaction mixture was than heated at 60°C on the water bath for 2-3 hrs and kept as such for 24 hrs, at ambient temperature . The precipitate were filtered and washed thoroughly with doubled distilled water and dried in an oven at 60°C. The dried product was ground and sieved with 100 mesh size
sieve. Therefore, metal ferrocyanide grains used for adsorption studies were comprised of particles up to 100 mesh size. Purity of metal ferrocyanides was checked by comparing the x-ray diffraction data of the complexes from literature. The relative intensity data and interplanar spacing [d]were also compared with reported values.

2.3. Spectral/ adsorption studies:
Ultraviolet absorption spectra of the various reaction mixture or elutes of some resulting products were determined by using JASCO UV/VIS -550 series spectrophotometer. Adsorption experiments of adenine were carried out with different metal ferrocyanides (Ni, Zn, Mn,Co,Cu)in triple distilled water. The concentration of different reaction solutions were observed by using JASCO, V-550 UV spectrophotometer and pH was measured in a digital pH meter. Metal ferrocyanides were repeatedly washed with distilled water and dried at 25°C before using.

Adsorption of adenine was studied as a function of pH and concentration of adsorbate. Therefore, adsorption of varying concentrations (7X 10^{-3} -1X10^{-5}) on different metal ferrocyanides over a range of pH between 4-9 was studied by adding appropriate buffer to 5 ml of solution of adsorbate in order to obtain saturation point. Acetate buffer and borax buffer (2N acetic acid and 2N sodium acetate) and(2 N boric acid and .05 M borax) were used to maintain pH in the range 3.6- 5.5 respectively. Buffered solution of adsorbate (6ml) was added to metal ferrocyanides (50mg each) in separate ground glass conical flasks (50ml). The flasks were capped and the content were stirred mechanically for 20 minutes. These were allowed to stand at room temperature for 7 hours. Similar sets adenine (nucleic acid bases )were incubated at different temperatures and pH to find out the condition of maximum adsorption. After about 7 hours, the experimental solution containing different adsorbents were centrifuged at 3000rpm for 15 minutes.

The concentration of all adsorbates used were determined by UV spectrophotometer at wavelength of maximum adsorption of respective adsorbate. The amount of adsorbed adenine were calculated by difference between the initial concentration and the amount adsorbed before and after adsorption. The amount adsorbed were used to obtain the adsorption isotherm. Adsorption studies of amino acids, nucleic acid bases and pentose sugar were studied on metal Ferrocyanide in double distilled water. All the investigations are carried out under a range of different concentration, temperature and pH. The concentration of the reaction solution after adsorption were recorded by using JASCO-V550 UV spectrometer and pH was measured in a digital pH meter. Metal ferrocyanides was repeatedly washed with distilled water and dried at 25°C before use and 50mg of the supernatant were centrifuged at 3000 rpm for 15 minutes. The equilibrium concentration of each adsorbate and the respective quantity adsorbed were used to obtain the adsorption isotherms. The amount of adsorbate in all cases studied related to the adsorption. However, interaction of metal ferrocyanides depends on some factors like ionic strength or orientation at sites for interaction with metal ferrocyanides surface. The results recorded in table 01 show an increase/decrease in % binding in presence of metal ferrocyanides. The equilibrium concentration of adenine and the amount adsorbed per gram of adsorbent were used to obtain the adsorption isotherm (fig.2 and 3).From the figures it appears that the amount of adenine adsorbed increase as their equilibrium concentration increases in solution becomes independent of the concentration. Initially, the curve shows linear relationship between amount adsorbed and saturation equilibrium concentration, whereas at higher concentration, saturation point occurs and no adsorption takes place. The asymptotic nature of adsorption isotherm suggested Langmuir type adsorption or monolayer formation given as:

\[
\text{Ceq} = \frac{1}{K_L \cdot X_m} + \text{Ceq} \cdot X_m
\]

where:

- Ceq = Equilibrium concentration of adenine
- K_L = Constant related to the heat of adsorption or enthalpy
- X_m = Amount of adsorbate (mg) adsorbed per gram of adsorbent

It was observed that adsorption trend (% binding, values of Langmuir constants) of adsorbate adsorbed on metal ferrocyanide depend on the nature of adsorbate as well as adsorbent. Adsorption of adenine are recorded in table 01. in terms of % binding. Percent binding has been calculated with the help of optical densities of the respective biomonomer solution before and after adsorption corresponding to saturation point on the curves. The % binding of adenine appear to have the following:

Ni[Fe(CN)6] > Zn2[Fe(CN)6] > Mn2[Fe(CN)6] > Co2[Fe(CN)6] > Cu2[Fe(CN)6]
Thus the addition of different metal ferrocyanides the adsorption throughout the entire concentration range of the isotherm. This shows that the increase in metal ferrocyanides strength increases the attractive force between the adenine and metal ferrocyanides. On the basis of observations the main role of inorganic cations in the adsorption on clay may be accounted as the neutralization of the negatively charged surface of the metal ferrocyanide. The Xm values recorded in table 02 reveal that the effect of metal ferrocyanides on adsorption of adenine for monolayer formation was relatively significant.

**Table -1 Percent binding of adenine on different metal ferrocyanides**

<table>
<thead>
<tr>
<th>M.F</th>
<th>Ni₂FC</th>
<th>Zn₂FC</th>
<th>Mn₂FC</th>
<th>Co₂FC</th>
<th>Cu₂FC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAB</td>
<td>38.25</td>
<td>38.06</td>
<td>37.70</td>
<td>33.51</td>
<td>32.96</td>
</tr>
</tbody>
</table>

FC= Fe(CN)₆, MF= Metal ferrocyanides, NAB, Nucleic acid bases

\[ \text{%binding} = \frac{\text{Conc. before adsorption} - \text{Conc. after adsorption}}{\text{Conc. before adsorption}} \times 100 \]

**Table -2 Langmuir constants for adsorption of adenine on different metal ferrocyanides**

<table>
<thead>
<tr>
<th>Type of adsorbent</th>
<th>Langmuir Constants</th>
<th>Adenine</th>
<th>Xₘ (mgg⁻¹)</th>
<th>Kₐ (Lmg⁻¹)</th>
<th>r² (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₂Fe(CN)₆</td>
<td>31.07 x 10²</td>
<td>7.51</td>
<td>0.997</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn₂Fe(CN)₆</td>
<td>31.86 x 10²</td>
<td>7.35</td>
<td>0.997</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn₂Fe(CN)₆</td>
<td>29.85 x 10²</td>
<td>4.69</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co₂Fe(CN)₆</td>
<td>27.74 x 10²</td>
<td>12.65</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₂Fe(CN)₆</td>
<td>27.24 x 10²</td>
<td>8.62</td>
<td>0.998</td>
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</tbody>
</table>

4. Acknowledgement
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5. References: