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Behavior of Poly-A onto Kaolin

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ABSTRACT

A combination of geochemical variables is necessary to explain the origin of life on Earth. Thus, in this work the sorption of Poly-A on a clay mineral (kaolinite) was studied to get an insight about the sorption capacity at different times and pH values, as well as to confirm the capabilities of the clay to protect the sorbate from an external source of ionizing radiation. Poly-A presented a high percentage of sorption in the clay, especially in acidic environments, and this percentage sharply decrease in alkaline media. On the other hand, Poly-A's recovery was higher in the system with clay, confirming its protection role.

1. Introduction

Chemical evolution is a hypothetical process postulated to explain the formation of bio-organic molecules via the action of energy sources that could have caused chemical reactions in the primitive Earth and led to a period of synthesis and subsequent accumulation of organic material that preceded life's possible origin [1]. One hypothesis for the origin of life on Earth is a gradual transition from an environment of inorganic compounds yielding simple organic components (such as CH4, NH2, etc.) to an environment with complex biomolecules and polymers [2].

Experimental simulations of primitive Earth's possible conditions, in which all these events took place, help in studying the formation process of these molecules and could help us understand the first steps in the origin of life. One of the most important aspects is the relationship between chemical evolution and geologically relevant scenarios. In this regard, the contribution of solid surfaces-such as silicates, carbonates, sulfides and clays-may have been important [3].

Another consideration in chemical evolution is the source of energy for these processes. One main source of energy was ionizing radiation, which could have a critical role because of its high energy deposition and penetration power. This energy source interacts with chemical

compounds to present changes that promoted an increase in organic material's complexity and diversity; it could also explain the decomposition patterns of some biomolecules [1].

In the chemical evolution process, the minerals present in the geological scenery, such as the clays, may have played a very important role in the formation of organic molecules due to their characteristics of absorbing, concentrating, protecting, and catalyzing the reactions of organic compounds [4].

Poly A is an important molecule in chemical evolution because it is an analog for nucleic acids in the steps from forming simple molecules to forming highly complex molecules, such as the informative-type RNA [5]. Gilbert proposed "the RNA world" an early period of Earth approximately 4 billion years ago in which RNA or some chemically similar molecule played a very important role in metabolic processes and in processing necessary information so other biologically important molecules and, later, the first simple organisms [6]. This molecule's catalytic and informative properties were key for processes that led to living beings. Coupled with this is the most attractive hypothesis, which suggests that adsorption to a specific surface of a mineral could be oriented by activating nucleotides and thus catalyzing a highly stereospecific reaction [7].

On the other hand, solid surfaces, such as clay minerals, may have an important role in prebiotic processes. The clays are constituted by aggregates of hydrated aluminum-silicates and have very variable compositions. With large surface and internal spaces or voids, their shape and properties depend on the type of clay in question [8].

Kaolin is a mineral found in the first ten meters of the continental crust. The kaolin is mainly composed of kaolinite, (sometimes halloysite), which is produced from mineral deposits with a significant amount of kaolin. It is a laminar silicate with two basic units that constitute its structure: SiO_4 tetrahedra and Al_2O_3 octahedra. The silicon layer shares free vertices with the oxygen in the aluminum layer. The layers of silicon and aluminum fit together. The result is a double Si/Al layer that is coupled with others to form the kaolin structure [9].

Minerals may have been key for prebiotic synthesis, leading researchers to include them in experiments carried out in heterogeneous systems exposed different energy sources. These studies focus on the behavior of biological molecules in the presence of some minerals to study the protective capacity they may provide under certain conditions [10]. In previous studies on the adsorption of nucleotides in clays such as montmorillonite, these mineral surfaces provided protection against radiation to prevent their degradation [11]. With RNA polynucleotides, sodium montmorillonite's protective capacity against external radiation sources has also been proven, increasing the chances of recovery of Poly-A compared to an absence of clay [12].

This work aims to test the capacity of adsorbing Poly A onto kaolin and to study the protector role of kaolin toward the irradiation of the Poly-A kaolin system at high doses of gamma irradiation.

2. Materials and Method

2.1 Preparation of Solutions

Using tridistilled water, Poly-A solutions (SIGMA Chemicals, USA) at a concentration of 5 mg/25 mL were prepared.

2.2 Adsorption experiments

For each solution, 0.10 g of kaolin obtained from the University of Missouri's Clay Minerals Repository in the USA was added to 3 mL aliquot solutions of Poly-A in a glass tube. The pH of the solutions was adjusted to 2, 4, 6, and 8 with HCl or NaOH, and the tubes were stirred for 15 minutes then centrifuged at 26,000 rpm for 30 minutes. The supernatant was separated and analyzed to determine the adsorption percentage.

Desorption of the polynucleotide was performed by adding the clay to an aqueous solution of NaOH at pH 8 while the samples were continuously stirred and centrifuged. Adsorption and desorption supernatants were analyzed by spectroscopy with a UV-vis detector at $\lambda = 260$ nm.

2.3 Irradiation of samples

At various times, irradiation was carried out in a 60 Co Gamma source (Gamma beam 651 PT) at ICN-UNAM at a dose rate of 158 Gy/min. The solutions were at pH 2 in oxygen-free solutions and in the presence and absence of clay.

2.4 Data Analysis

The obtained percentages of the clay's adsorption and desorption at different pH ranges are presented in graphs showing the trends of polynucleotide behavior. After submitting the samples to the radiation, the dose/response relationship was observed, and the percentage amounts of unaffected Poly-A were compared to determine the kaolin's protective capacity.

3. Results and discussion

3.1 Adsorption Experiments

Changes in the pH of the solution affected the clay's adsorption capacity. Concerning the pH variations in the solution, 98% of the Poly-A was adsorbed at pH 2 and 40% at pH 8. This can be observed in the Figure 1 at fix agitation time. The tendency to decrease the adsorption percentage as the environment becomes more alkaline should be highlighted [13].

Figure 2 shows the adsorption in an acid medium. The kaolin presented a very high and significant adsorption capacity, with maximum adsorption levels greater than 95% in short agitation periods that did not exceed 15 minutes and remained constant.



Figure 1: Adsorption of Poly-A at different pH and a fix agitation time.



Figure 2: Adsorption of Poly-A on kaolin at pH 2.

Purines, pyrimidines, and nucleosides require adsorption conditions with an acidic pH around 2.5 [14]. Thus, to explain the adsorption capacity of the Poly-A system on kaolin, an acidic pH is necessary because the molecules are protonated at this pH, and the adsorption occurs mainly in the octahedral surface hydroxyls via hydrogen bridges of the crystal or with the tetrahedral side through hydrogen bonds [13-15].

The mechanism of adsorption of organic molecules by means of clays is a complex phenomenon, one of these is that they act as an ion exchanger due to their excess surface charge. The adsorption depends on the conditions of the medium, such as the properties of the molecule, the concentration, the type of clay and the pH, with respect to the latter it has been observed that in the case of bio-organic compounds the adsorption is greater in acidic conditions [16].

When treating the clays from previous samples for desorption, 50–65% of Poly-A was desorbed from the clay under alkaline conditions at pH 8. See Figure 3.



Figure 3: Poly-A desorption at different pH values.

3.2 Irradiation Experiments

The results indicate that Poly-A's degree of decomposition increases as the exposure time and gamma radiation dose increase, but the decomposition decreases in the presence of clay at the same irradiation dose as the samples without clay. The Poly-A was irradiated in different doses to observe the irradiation doses effect. Figure 4 shows that, at irradiation doses 16 kGy, 71% of Poly-A was still observed, and almost 100% was present in the presence of clay, denoting that the kaolin can almost completely protect the molecule at that radiation dose. At 33 kGy, however, the solution without clay of Poly-A noticeably decomposes to 19%; but with clay, a presence of 44% is recorded. This protective effect is still under study, and energy transfer processes may be the responsible for the observed behavior of the polymers in the kaolin at the surface, allowing the Poly-A to interact with the medium and providing only partial protection. Comparing these results with others obtained with montmorillonite where it has been observed that adsorption is carried out at the edges of the crustal structure with doses equal to those presented in this work [12].



Figure 4: Radiolysis of Poly-A with and without kaolin (normalized values).

Kaolin has been shown to serve as a catalyst for the synthesis or polymerization of various types of organic molecules, including purines and pyrimidines [17].

Conclusions

Kaolin was shown to have a high adsorption capacity under acidic conditions for the Poly-A polymer and this capacity is affected by pH. The clay has a partially protective capacity when Poly-A is exposed to a high energy source, as compared to Poly-A without the presence of the clay.

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