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**Original Article**

## Role of clay organic matter complex to determine the soil capacity

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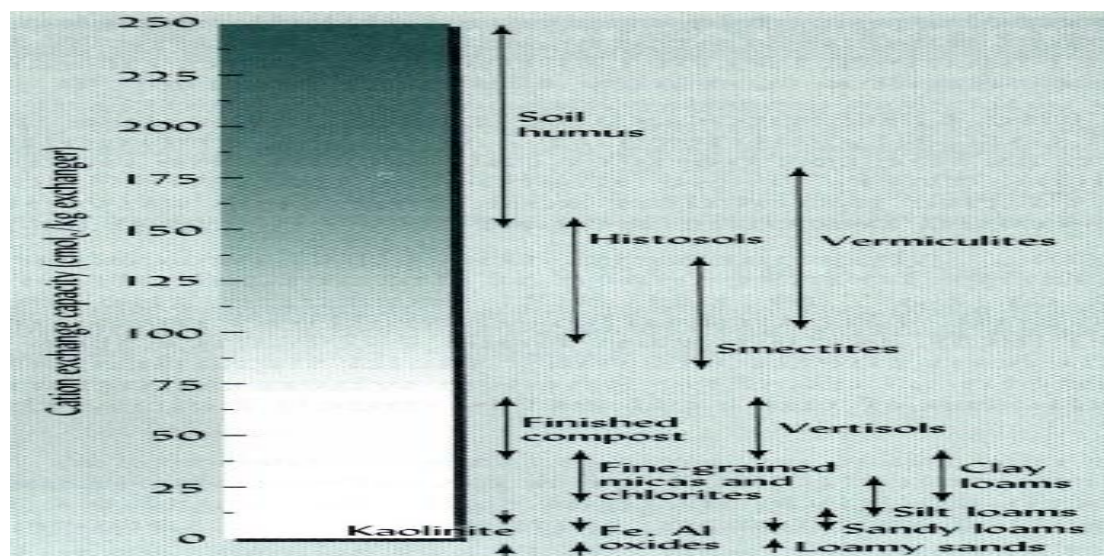
**ABSTRACT**

Soil may hold humus by five different mechanisms: simple isolated masses of humus, insoluble metal complexes, humus held on positively charged spots in the soil, humus in or on clay interlayers, and humus in or on silicates soluble in cold dilute hydrofluoric acid. The first humus group can sometimes be separated from the main mass of the soil by a flotation technique. The second group, which may sometimes include the first, can only be dispersed when the metals have been replaced by, say, sodium ions, which can be done by treating the soil with a salt whose anions form stable soluble complexes with the metallic ions responsible and which can be done equally well by the use of suitable cation-exchange resins. The third group is displaced by sodium hydroxide, for the alkalinity of this solution decreases the positive charges on the mineral colloids, but because it increases the negative charges on the humus, it will also disperse humus held by other mechanisms. Hadding (1923) and Rinne (1924) were the first to apply X-ray diffraction analyses to the study of clays. They were able to show that clays were, in the main, composed of crystalline materials, a conclusion which ran counter to opinions currently held at that time. Some six years later, Pauling (1930a; 1930b) published the results of his classical X-ray diffraction studies on the micas, talc, pyrophyllite, chlorite, and kaolinite, together with those on cristobalite (SiO<sub>2</sub>)' gibbsite (Al(OH)<sub>3</sub>), and brucite (Mg(OH)<sub>2</sub>). Condensation in a 1: 1 proportion gives rise to the two-sheet or dimorphic type minerals exemplified by kaolinite. Similarly, the three-sheet or trimorphic clays are formed by a 2: 1 condensation, the octahedral Al (OH) 6 sheet being sandwiched between two tetrahedral sheets, e.g., pyrophyllite. Little can be said about the fourth and fifth mechanisms—that is, the humus released by hydrofluoric acid—but it may include an important part of the clay-humus complex.

**Key words:** Soil, Clay, Organic matter and Humus

**INTRODUCTION**

The organic matter content of sands may be less than 1%; loams may have 2% to 3%, and clays from 4% to more than 5%. The strong chemical bonds that develop between organic matter and clay and fine silt protect organic molecules from attack and decomposition by microorganisms and their enzymes. "Clay associated organic matter as all organic matter present in the clay-sized fraction, both free organic particles and organic matter bound to minerals". Primary structure of soils as defined by the soil texture resulting from the association of organic matter (OM) with primary mineral particles, and as complexes that are isolated after complete dispersion of soils. The chemistry of clay-organic reactions dates only from the early 1940s, following closely on the general acceptance of the crystallinity, and the elucidation of the structures, of the main group of clay minerals. This is not to say, however, that before this time people were unaware of the existence of some kind of association between clays and organic substances. The early soil chemists for example, rightly postulated complex-formation between the clay fraction and the organic constituents of soils as being responsible for the stability and resistance to microbial decomposition of humus. Humus is a complex and rather resistant mixture of brown or dark brown amorphous and colloidal organic substance that results from microbial decomposition and synthesis and has chemical and physical properties of great significance to soils and plants. Similarly, the ability of clays to decolourise oils and clarify wines has been known for a very long time. Indeed, the use of water slurries of crude clays for adsorbing wool grease can be traced to biblical times. This process, known as fulling, gave rise to the familiar term "fuller's earth".



### Cation Exchange Capacity

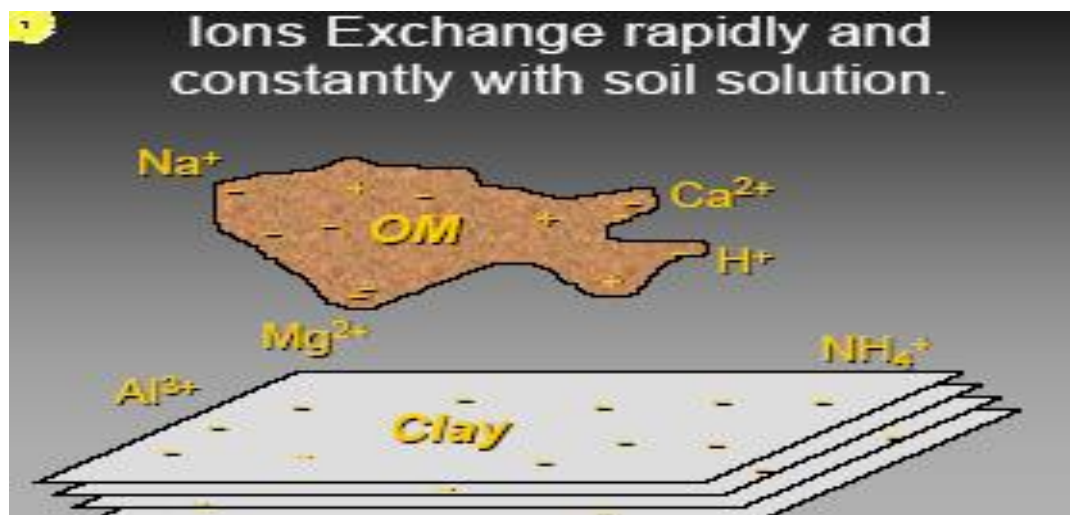
#### Nature of clay organic matter complex

- ✓ Clay organic matter complex enriched in top soils are the main reservoirs of plant nutrients.
- ✓ Clay organic matter complex are the adsorption products between the organic cations anions or molecules transferred from solution, liquids or gaseous states to clay surface generally due to the physical or chemical bonds.
- ✓ Clay organic matter complex are conglomerate soil colloids in which clay, organic/hydroxides (including sesquioxides and allophanes) and humic material remain associated.
- ✓ The type and amount of layer silicates, intercalation of OM, content of pedogenic oxides, soil properties, vegetation, etc are decisive in the formation of clay- organic bonds.

#### Complex formation between clay and organic substance

- ✓ One of the processes of linking OM to clay particle (C) through polyvalent cations and represented as  $[(C-P-OM)_x]_y$ . Several other modes of interaction like water bridging, ligand exchange, hydrogen bond, etc.

The type and amount of layer silicates, intercalation of OM, content of pedogenic oxides, soil properties, vegetation, etc. are decisive in the formation of clay-organic bonds. Fractions rich in Kaolinite often showed less carbon contents, the smectite -rich fractions contain organic carbon within a wide range while the fraction dominated by allophane have the largest carbon contents. Kang and Xing reported the sorption of relatively low molecules fractions of humic acid (HA) on goethite surface leading to fractionation. Study of complex formation between clay and organic substance has been approached from essentially two directions. The first involved isolation and separation of complex from soils based on size and density followed by their characterization. The interaction process may be studied by allowing organic substance and their fraction to react with known clay species and examining the resulting complexes. It is evident that various clay minerals can bind humus substances through some linkages known as clay-humus complex. Many investigators consider that the complexes between humus substances and clays are probably formed by bridging through the exchangeable cations like Ca, Mg and Al. Besides this, they also consider that humus substances penetrate into the inner layer space of the crystalline clay mineral lattice. Another mechanism for the formation of stable clay-humus complexes are associated with the help of sesquioxides, which make specific bridges between humus substances and the crystalline lattice of clay minerals. Presumably these bridges are complex Al and Fe- humus compounds with non-silique forms of sesquioxides. They are fixed to the surface of the clay minerals during dehydration by a process of adhesion at the expense of inter molecular types of linkages.



**Forces involved in the interaction between clays and organic compound (Greenland, 1965)**

**1. Coulombic attractions between**

- a. Negatively charged surface and positively charged organic compound
- b. Positively charged surface, or ion or oligo-ion at surface, and organic anion.

**2. Van der Waals forces, composed of**

**a. Polar**

- i. Charged-dipole interactions
- ii. Dipole-dipole interactions
- iii. Charge induced dipole interaction
- iv. Dipole-induce dipole interactions

**b. Non-polar**

- i. Dispersion forces

**There are two types of linkage take place during the interaction of clay with humic acids:**

Unstable-type of linkage, humic acid is arranged on the external micelle surface of the clay; this humic acid is easily extracted by alkali. Stable-type of linkage, (humic acid is not extracted by alkali), is formed from the interaction of clay, humic acid and the exchangeable cations ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  occurring in the lattice of the clay mineral; the OH and COOH groups in the humic acid take part in the linkage.

**Hydrophobic bonding on clay - organic complexes**

Natural clay-organic complexes may have adsorption properties quite different from pure clays. Many organic molecules, including aromatics and particularly the halogenated types such as chlorinated and brominated phenyls and biphenyls, are adsorbed a little, if at all, on clay surfaces. The surfaces of clays can be made hydrophobic after reaction with organic molecules which have some hydrophobic properties. When this happens, the surfaces of clay-organic complexes are become hydrophobic and in turn organo-philic. Therefore, hydrophobic portions of the organic adsorb ate can react with the hydrophobic organic portions of clay-organic complexes.

**Formation of Complexes**

Interlayer complexes of clays with simple organic compounds are essentially of two types.

- (1) As a cation,
- (2) As a polar non-ionic compound.

The first type of complex may arise either from replacement of the inorganic cations, initially occupying exchange positions, by organic cations, or from protonation at the clay surface of absorbed organic bases. The second type may be formed by replacement of either the interlayer water or of a previously intercalated organic liquid. In complexes involving kaolinite, the polar compound may intercalate directly from the liquid, from the melt, or from its aqueous solution.

**Complexes with Organic Anions**

As might be expected, anionic compounds are largely repelled by negatively charged clay surfaces and little or no adsorption occurs. Polyvalent cations occupying exchange positions or water molecules co-ordinated to such cations may act as a bridge between the organic anion and the

clay surface. The adsorption of humic and fulvic acids by clays may take place through this type of interaction.

- ✓ Cations are attracted to the clay particles.
- ✓ These cations are held on the clay surface electro statically.
- ✓ They are held by small particles of clay and organic matter.
- ✓ These small particles are called micelle (Micro cell).
- ✓ Ions that are held very lightly with the colloids may be trapped between layers of clay micelle.
- ✓ When any cation is added to the soil such as  $\text{Ca}^{++}$ ,  $\text{K}^+$  or  $\text{NH}_4$  through fertilizers and soil amendments they are exchanged with ions held on the colloids.
- ✓ For Montmorillonite, the affinity of the organic ion for the clay increases regularly with molecular weight, that is, the larger the cation the stronger its adsorption.

### **Role of bio-organic compound in clay organic matter complex**

Because of their importance to organic-matter transformations in soils, the interactions of clays with amino acids, purines, pyrimidines, nucleosides, proteins, and nucleic acids have received much attention. Amino acids exist as cations under acid conditions and hence their adsorption by clays occurs largely through an ion-exchange process. At or close to the isoelectric pH, these compounds exist as dipolar ions, and ion-dipole together with hydrogen-bonding-type interactions are predominant. Very little adsorption occurs at alkaline pH, since amino acids are negatively charged under these conditions. Similarly, the interaction of purines, pyrimidines, and nucleosides with clays is pH-dependent, and steric factors related to molecular geometry and aromaticity are also important. Proteins and nucleic acids are rapidly adsorbed by clays; the amount retained decreasing with an increase in pH. Formation of interlayer complexes may partly "protect" these compounds from microbial degradation.

### **Conceptual models of clay-organic complexes**

The conceptual models assumes that SOM consist of a heterogenous mixture of compounds that display a range of amphiphilic or surface like; properties, and are capable of self-organization in aqueous solution. **Bilayer model of clay** - organic interactions, sharply contrasted with the traditional view of clay-organic interaction, which were visualized as associated of large, multifunctional polymers with mineral surface via broad model postulated that decayed organic materials are often bound to clay surfaces by amino acids or proteins. The **zonal models** was developed by Kleber et al. based on the amphiphilicity of SOM fragments, and the intimate involvements of proteinaceous compounds in organo-minerals associations. **Zonal concept** proposes that the self-assembly of SOM on clay mineral surfaces creates a layered or zonal structure with regular features.

### **Importance**

1. Clay associated organic matter refers to organic matter bound to clay mineral surfaces. For example: Ca bridging, or intercalation between clay layer (Theng and Tate, 1989).
2. It is practically defined fractionation of the clay size fraction.
3. Secondary organo-mineral associations, often referred to as aggregates (Christensen, 1996) are involved in the physical protection of organic matter by occlusion.
4. To examine the composition of clay - associated organic matter, it is necessary to separate it from the clay matrix, e.g. by extraction. Such as  $\text{H}_2\text{O}$ ,  $\text{NaOH}$  followed by  $\text{N}_4\text{P}_2\text{O}_7$ , and *n*-hexane.
5. This largely depends on the type and amount of clay minerals, and may also be affected under different nutrient management options over a long-term period.

### **Conclusion**

Humus contains many useful nutrients for healthy soil. One of the most important is nitrogen. Nitrogen is a key nutrient for most plants. Agriculture depends on nitrogen and other nutrients found in humus. The particles of these soils are tightly packed together with each other with very little or no airspace between them. This soil is known for very good water storage qualities and makes it hard for moisture and air to penetrate it, making it easier for crops to grow. Silt is like clay in that it retains moisture but doesn't allow much oxygen flow. Silt deposits can be very fertile and support lots of plant growth like the wetlands around the Mississippi River or rich farming near the Nile River in Egypt. Clay soils provide a wonderful foundation for plants by anchoring roots securely in the soil. Many perennials and annuals thrive in clay soils since they can get a firm grip on the soil with their roots. This firm grip allows them to survive extremes of temperature and moisture that plants grown in sandy soil cannot.

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