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Soil Colloids: Properties, Nature, Types and Environmental Significance of Humic Substances

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C oil colloids are critical components of soil, possessing unique properties due to their extremely fine particle size and high surface area. These colloids include particles smaller than 0.002 mm, with colloidal properties becoming prominent in particles under 0.001 mm. Soil colloids exhibit several distinguishing properties: they have substantial surface areas, carry surface charges that attract ions, and adsorb water molecules, which contribute significantly to soil's physical and chemical behaviour. The high surface area and surface charges allow soil colloids to attract cations, forming a double layer of ions that impacts nutrient availability. Soil colloids also display cohesion and adhesion, which influence soil structure and water retention, as well as swelling and shrinkage properties, particularly in clays like smectite, which expand when wet and shrink when dry. There are four main types of soil colloids: layer silicate clays, iron and aluminium oxide clays, allophane and amorphous minerals, and humus. Each type has distinct chemical compositions and physical characteristics. Silicate clays, such as phyllosilicates, are structured in layers and exhibit high cation exchange capacity (CEC), essential for nutrient exchange in soil. Iron and aluminium oxide clays, common in highly weathered soils, are generally non-swelling and possess high phosphorus adsorption capacity. Amorphous minerals, such as allophane, frequently occur in soils derived from volcanic ash and have variable charge properties dependent on soil acidity. Humus, an organic colloid, consists of decomposed organic matter rich in carbon, hydrogen, and oxygen, and contributes significantly to soil's cation exchange capacity due to its abundant negative charges. The interactions of these diverse colloids profoundly influence soil fertility, structure, and overall soil health, making them essential for sustainable soil management and crop productivity.

Keywords: Soil colloids, colloidal state, zeta potential, cohesion, adhesion, dispersion, flocculation, phyllosilicates, and humus

Soil Colloids

The colloidal state refers to a two-phase system in which one material in a very finely divided state is dispersed through second phase. The examples are: Solid in liquid (Dispersion of clay in water) and Liquid in gas (Fog or clouds in atmosphere). The clay fraction of the soil contains particles less than 0.002 mm in size. Particles less than 0.001 mm size possess colloidal properties and are known as soil colloids.

General Properties of Soil Colloids

1. Size: The inorganic and organic colloids are extremely small size - smaller than 2 micrometers in diameter. These particles cannot be seen using an ordinary light microscope but can be seen only with an electron microscope.

- 2. Surface area: Because of their small size, all soil colloids have a larger external surface area per unit mass. The external surface area of 1 g of colloidal clay is 1000 times that of 1 g of coarse sand. Certain silicate clays have extensive internal surfaces occurring between plate like crystal units that make up each particle and often greatly exceed the external surface area. The total surface area of soil colloids ranges from 10 m²/g for clays with only external surfaces to more than 800 m²/g for clays with extensive internal surfaces. The colloid surface area in the upper 15 cm of a hectare of a clay soil could be as high as 700,000 km² g¹1.
- **3. Surface charges:** Both external and internal surfaces of soil colloids carry negative and/or positive charges. Most of the organic and inorganic soil colloids carry a negative charge. When an electric current is passed through a suspension of soil colloidal particles they migrate to anode, the positive electrode indicating that they carry a negative charge. The magnitude of the charge is known as *zeta potential*. The presence and intensity of the particle charge influence the attraction and repulsion of the particles towards each other, there by influencing both physical and chemical properties. The sources of negative charge on clays comes from
- i) Ionizable hydrogen ions: These are hydrogen from hydroxyl (OH) ions on clay surfaces. The -Al-OH or -Si-OH portion of the clay ionizes the H and leaves an un-neutralized negative charge on the oxygen (-AlO or SiO). The extent of ionized hydrogen depends on solution pH and hence these negative charges are *pH dependent charges*. More ionization occurs in alkaline (basic) solutions.
- **ii)** Isomorphous substitution: This is due to the substitution of a cation of higher valence with another cation of lower valence but similar size in the clay crystal structure. In clay crystals some ions fit exactly into mineral lattice sites because of their convenient size and charge. Dominantly, clays have Si⁴⁺ in tetrahedral sites and A1³⁺ in octahedral sites. Other ions present in large amounts during clay crystallization can replace some of the A1³⁺ and Si⁴⁺ cations. Common substitutions are the Si⁴⁺ replaced by A1³⁺, and replacement of A1³⁺ by Fe³⁺, Fe²⁺, Mg²⁺ or Zn²⁺. As the total negative charge from the anions (oxygen) remains unchanged, the lower positive charge of the substituted cations results in excess negative charges on clay crystals.
 - **4. Adsorption of cations**: As soil colloids possess negative charge they attract and attach the ions of positive charge on the colloidal surfaces. They attract cations like H⁺, A1³⁺, Ca²⁺ and Mg²⁺. This gives rise to an ionic double layer. The Isomorphous substitution in the colloidal particle makes the external and internal layers of clay minerals negatively charged and these surfaces act as huge anions, which form the inner layer of the double layer. The outer layer is made up of a swarm of loosely held (adsorbed) cations attracted to the negatively charged surfaces.
 - **5. Adsorption of water**: A large number of water molecules are associated with soil colloidal particles. Some water molecules are attracted to the adsorbed cations and the cation is said to be in hydrated state. Others water molecules are held in the internal surfaces of the colloidal clay particles. These water molecules play a critical role in determining both the physical and chemical properties of soil.
 - **6. Cohesion**: (Attractive force between similar molecules or materials). Cohesion indicates the tendency of clay particles to stick together. This tendency is due to the attraction of clay particles for water molecules held between them. When colloidal substances are wetted, water first adheres to individual clay particles and then brings about cohesion between two or more adjacent colloidal particles.
 - **7. Adhesion**: (Attractive force between different molecules or materials). Adhesion refers to the attraction of colloidal materials to the surface of any other body or substance with which it comes in contact.

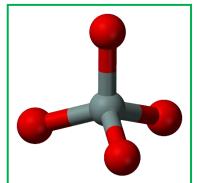
- **8. Swelling and shrinkage**: Some soil clay colloids belonging to smectite group like Montmorillonite swell when wet and shrink when dry. After a prolonged dry spell, soils high in smectite clay (e.g. Black soil -Vertisols) often show crises-cross wide and deep cracks. These cracks first allow rain to penetrate rapidly. Later, because of swelling, the cracks will close and become impervious. But soils dominated by kaolinite, chlorite, or fine-grained micas do not swell or shrink. Vermiculite is intermediate in its swelling and shrinking characteristics.
- **9. Dispersion and flocculation**: As long as the colloidal particles remain negatively charged, they repel each other and the suspension remains stable. If on any account they loose their charge, or if the magnitude of the charge is reduced, the particles coalesce, form flock or loose aggregates, and settle down. This phenomenon of coalescence and formation of flocks is known as flocculation. The reverse process of the breaking up of flocks into individual particles is known as de-flocculation or dispersion.
- **10. Brownian movement**: When a suspension of colloidal particles is examined under a microscope the particles seem to oscillate. The oscillation is due to the collision of colloidal particles or molecules with those of the liquid in which they are suspended. Soil colloidal particles with those of water in which they are suspended are always in a constant state of motion. The smaller the particle, the more rapid is its movement.
- 11. Non permeability: Colloids, as opposed to crystalloids, are unable to pass through a semi-permeable membrane. Even though the colloidal particles are extremely small, they are bigger than molecules of crystalloid dissolved in water. The membrane allows the passage of water and of the dissolved substance through its pores, but retains the colloidal particles.

Types of Soil Colloids

There are four major types of colloids present in soil

1. Layer silicate clays: These important silicate clays are also known as phyllosilicates (Phyllon - leaf) because of their leaf-like or plate-like structure. These are made up of two kinds of horizontal sheets. One dominated by silicon and other by aluminum and/or magnesium.

Silica tetrahedron: The basic building block for the silica-dominated sheet is a unit composed of one silicon atom surrounded by four oxygen atoms. It is called the silica tetrahedron because of its four-sided configuration. An interlocking array or a series of these silica tetrahedra tied together horizontally by shared oxygen anions gives a tetrahedral sheet (Figure 1).



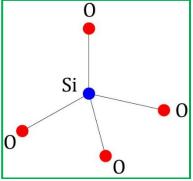


Figure 1: Silica tetrahedron

Alumina octahedron: Aluminum and/or magnesium ions are the key cations surrounded by six oxygen atoms or hydroxyl group giving an eight-sided building block termed octahedron. Numerous octahedra linked together horizontally comprise the octahedral sheet (Figure 2). An aluminum-dominated sheet is known as a di-octahedral sheet, whereas one dominated by magnesium is called a tri-octahedral sheet. The distinction is due to the fact that two

aluminum ions in a di-octahedral sheet satisfy the same negative charge from surrounding oxygen and hydroxyls as three magnesium ions in a tri-octahedral sheet.

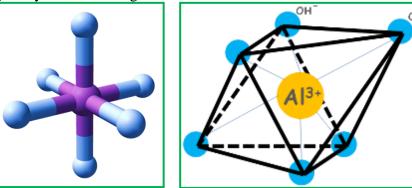


Figure 2: Alumina octahedron

The tetrahedral and octahedral sheets are the fundamental structural units of silicate clays. These sheets are bound together within the crystals by shared oxygen atoms into different layers. The specific nature and combination of sheets in these layers vary from one type of clay to another and control the physical and chemical properties of each clay.

- **2. Iron and aluminum oxide clays** (**sesquioxide clays**): Under conditions of extensive leaching by rainfall and longtime intensive weathering of minerals in humid warm climates, most of the silica and alumina in primary minerals are dissolved and slowly leached away. The remnant materials, which have lower solubility are called sesquioxide's. Sesquioxide's (metal oxides) are mixtures of aluminum hydroxide, Al (OH)₃, and iron oxide, Fe₂O₃, or iron hydroxide, Fe(OH)₃. The Latin word *sesqui* means one and one-half times, meaning one and one-half times more oxygen than Al and Fe. These clays can grade from amorphous to crystalline. Examples of iron and aluminum oxides common in soils are gibbsite (Al₂O₃.3H₂O) and goethite (Fe₂O₃.H₂O). Less is known about these clays than about the layer silicates. These clays do not swell, not sticky and have high phosphorus adsorption capacity.
- **3. Allophane and other amorphous minerals**: These silicate clays are mixtures of silica and alumina. They are amorphous in nature. Even mixture of other weathered oxides (iron oxide) may be a part of the mixture. Typically, these clays occur where large amount of weathered products existed. These clays are common in soils forming from volcanic ash (e.g., Allophane). These clays have high anion exchange capacity or even high cation exchange capacity. Almost all of their charge is from accessible hydroxyl ions (OH), which can attract a positive ion or lose the H⁺ attached. These clays have a variable charge that depends on H⁺ in solution (the soil acidity).
- **4. Humus (Organic Colloid):** Humus is amorphous, dark brown to black, nearly insoluble in water, but mostly soluble in dilute alkali (NaOH or KOH) solutions. It is a temporary intermediate product left after considerable decomposition of plant and animal remains. They are temporary intermediate because the organic substances remain continue to decompose slowly. The humus is often referred to as an organic colloid and consists of various chains and loops of linked carbon atoms. The humus colloids are not crystalline. They are composed basically of carbon, hydrogen, and oxygen rather than of silicon, aluminum, iron, oxygen, and hydroxyl groups.

The organic colloidal particles vary in size, but they may be at least as small as the silicate clay particles. The negative charges of humus are associated with partially dissociated enolic (-OH), carboxyl (-COOH), and phenolic groups; these groups in turn are associated with central units of varying size and complexity.

Difference between organic and inorganic colloids

Humus	Clay	
Made up of C, H and O	Made up of Si, Ai and O	
Complex amorphous organic colloid	Inorganic and crystalline	
More dynamic, formed and destroyed more rapidly	Clays are stable relatively	
Complex structure not well known	Clays have definite and well-known structure	

Significance of soil colloids

The organic and inorganic contaminates are often transported via colloidal particles. Majority of surface area and electrostatic charge in a soil resides in the less than I µm size fraction, with particles with radii between 20 and 1000 mm constituting the major part of soil surface area. Since major part of the surface area is in the colloidal fraction of the soil, almost all surface-controlled processes including adsorption reactions, nucleation and precipitation involve colloids. In addition to these chemical processes, colloids are mobile in soils, and thus affect not only the chemical transport of otherwise immobile chemicals, but also exert a strong influence on soil hydraulic properties.

What are Humic Substances chemically?

Chemically Humic Substances (HS) are the aggregates of sugars, fatty acids, polypeptides, aliphatic chains, aromatic rings and but specifically in literature humic substances are known as mixture of complex organic compounds viz., humic acid (HA), fulvic acid (FA) and humin. Humic substances are mostly widely spread natural complexing ligands occurring in soil, manures, wastes, natural water, lakes sediments, lignite's, peat, coal, sewage and geological organic deposits. Earth contains 25% carbon in HS of total organic carbon (TOC) of earth. The terrestrial media contain 80% in HS and aquatic media contain 60% in HS of their TOC. The strong alkali like NaOH, KOH and sodium pyrophosphate (Na₄P₂O₇) acts as extractant for HS. The structure of HS is till today not fully understood, it is under debate as HS have different functional groups like carboxylic, phenolic, carbonyl, hydroxyl, amine and amide and due to unique structure, properties and polyfunctional groups they act as strong or powerful chelating agents. Also due to zwitter ion characteristics of HS, they exhibit the ion exchange and also acts as adsorbent. Due to unique structures, chemical and biochemical properties of HS, they play very significant roles in area of agriculture (soil, crops and animal) industry, bio-medicine and environment.

Thus, HS commonly referred to as humus (HA, FA and humin) which are considered to play crucial roles in the terrestrial and aquatic or in environment affecting human health. Thus, study of HS in relation to environmental and human health is important.

Environmental Significance of HS

Sustainable quality food production with environmental security is only possible with healthy or quality soil. Soil health and its quality is only possible when it soil contain adequate amount of humic substances (HS) *i.e.*, humic acids (HA), fulvic acids (FA) and humin. Besides the soil fertility and crop nutrition, HS perform many functions in various life or natural cycles in earth; i.e., in environment.

After discovery of fertilizers and its continuous use without use of manures (source of HS) caused many serious sociological and ecological problems, which needs new approach of fertilization to crops by giving the higher priority to humus or humic substances addition along with fertilizers.

The agronomist and soil scientists have recognized the importance of HS in sustainable agriculture, achieving the expected food and environment security. To study and

understand the environmental (soil, water, climate, plant and animal) significance of HS, any learner has to study the basic concept of SOM and HS with respect to its structure, properties and its interaction in environment.

Basic concepts of humic substances

- They are bulk of soil organic matter.
- Terrestrial media (soil and land) contains 80% C in HS.
- Aquatic media contains 60% in HS.
- HS helps to improve soil fertility due to its role in stabilization of soil aggregates.
- In industry HS used as adsorbent (avoiding metal poisoning).
- Due to unique properties, it has great significance or application in environment.
- Structure of HS is still unknown.
- Functional groups present are: Carboxylic, phenolic, carbonyl, hydroxyl, amine, amide.
- Humic substances are aliphatic molecules.
- Due to presence of polyfunctional groups they act as strong or powerful chelating agents.
- They possess zwitter ion characteristics due to their both charges and possess CEC and AEC.
- It contributes 80% of soil organic matter (SOM).
- Most common elements in HS are: C, O, H, N and S.

Properties of HS (FA + HA + humin)

•	1 Toperties of 115 (FA + 11A + numin)								
Properties	Fulvic Acid	Humic Acid	Humin						
Solubility	Water soluble under acidic, neutral and alkaline conditions.	Water soluble in alkaline condition but not acid condition.	Not soluble regardless of pH conditions <i>i.e.</i> , insoluble in both, acid and alkali.						
Solubility in NaOH	Soluble	Soluble	Insoluble						
Molecular weight	Low	Medium	High						
Colour	Light yellow to yellow brown	Dark brown to black.	Dark black						
Structure	Simple, clear, and precise.	Moderately complex. 35% variable C ring structure, 65% stable Carbon chain structure.	Complex						
Oxygen content	High	Medium	Low						
Acidity	High 900-1400 mmol/100g	Medium 400-870 mmol/100g	Low						
Carbon content	Low	Medium	High						
Functional group	More number	Medium	Less numbers						
Reactivity	High	Medium	Low						
Size of molecule	Small	Medium	Large						
Mode of use	Foliar spray	Soil application though manures and fertilizers.	Soil application						

Role in soil quality	Food for microbes and improvement of biological properties	Chelating action and ion exchange	CEC and buffering capacity. WHC and structure of soils improved.
Elemental composition	C: 40-49%	C: 55-62%	C: >62%
	H: 3.5-5%	H: 3.5-5.5%	H: 5.5%
	O: 44-49%	O: 30-33%	
	N: 2-4%	N: 3.5-5%	
Degradation tendency	Easily degradable.	Moderately resistant.	Extremely resistant

Application or use of humic acid and fulvic acid to soil and crops proved their beneficial effects, however, the magnitude or significant effect of use or application of humic acid and fulvic acid is depends upon many factors such as:

- 1) Source of Humic substances
- 2) Crop or plant species.
- 3) Soil type
- 4) Method of application

Considering the properties and role of humic substances in soils and crops, integration of HS with fertilizers and their effects on soils and crops is matter of study and research.

- The main (\sim 70%) fraction of HS is humic acid or humate.
- Still chemically defined molecular structure of humic acid and fulvic acid has not been described.

At what pH the soil will be rich of humate?

Soil with a near neutral pH would contain high level of humate. On the contrary, soil with low pH would contain low amount of humate.

Formation of Humic substances

Humic substances are believed to be formed due to humification of SOM which brought by biochemical and microbial reactions.

- Can enhance the biotic and abiotic degradation of phenols, polyaromatic hydrocarbon (PAH) and pesticide in environment.
- Strong binding ability with metals involved in detoxification of some heavy and hazardous metals in environment.
- Significant role in environment pollution remediation because of its unique property of high ion exchange (both cation and anion).
- Humate can detoxify organic and inorganic inhibitors of biological processes.
- Humate enhance bio-degradation of some organic substances like phenol, formaldehyde and mineral oils.

Thus, humate can be potentially used as filler material which acts as barrier wall to prevent against heavy metals.

Role of HS in industry

- To control the setting rate of concrete.
- In preparation of quality leather, eg. Leather dye, tanning leather.
- Wood industry- furniture or colour
- Plastic industry- PVC pipes
- Preparation of new drugs or medicines.

Roles of HS in soils

• Significantly influence soil quality and productivity.

- Due to high base exchange capacity improves soil fertility.
- Additive in fertilizers for improving NUE.
- Chelating effects for Fe and some other micronutrients.
- Ca-humate important for soil.
- Humates can be used for remediation of pollution of soils with phenols, formaldehyde, excess phosphorous and some heavy metals eg, Pb, Hg, Al.
- HS increase the quality and productivity of soil by improving soil structure, water holding capacity or water retention capacity, ion exchange. They also block toxic or heavy metals in soils, avoid toxicity to microbes, plant and human health.

Roles of HS in plants

- Ammonium humate has its growth stimulating effect in plants.
- Na-humate is important for plant
- HS has positive effects on plant physiology by improving soil structure and fertility and by influencing nutrients uptake and architecture of plant.
- HS have been shown to contain some auxins and an "auxin-like" activity of HS has been reported.

Formation of humic substances or humus in soils

Humus formation study is very hard to understand, still this subject is long standing and not fully understood or clear.

Following are some theories of humus formation:

- 1. Lignin theory
- 2. Polyphenol theory
- 3. Sugar-amine condensation theory

Origin of humus formation or synthesis start from lignin. Polyphenols are the precursor for synthesis of humic acid (HA). Various components involved in humification: Amino acids, lignin, CHO. Intermolecular forces involved in humification: Donor-acceptors, ionic hydrophilic, hydrophobic. Lignin is main component involved in synthesis of humus, besides lignin and its nature, other components (CHO, polyphenols, sugar, amino, other biomolecules) vary with types of SOM (originated plant + MO + Animal or their residues) and other physical, chemical, microbial, geographical and climatic conditions decide the mechanisms (theory/pathway) of humus formation.

Why humic acid has ability for ion exchange, complex formation and oxidation-reduction reaction?

Humic acid molecules contain COOH, phenolic, amino acid and quinone functional groups with aromatic nucleus of low degree of condensation. The mobile p-type electrons in aromatic nucleus and various functional group present in humic acid molecule cause the ability of ion-exchange, complex formation and oxidation-reduction reactions.

When humic acid molecules in soil will act as an acid and as humate?

Humic acids are colloids and behave somewhat like clays. When cations sites of the humic acid molecule are filled predominantly with hydrogen cations, the material is considered to be an acid, on the contrary when the predominant cations on exchange site is other than hydrogen, the material is called as humate.

The humate of monovalent alkali metals (Na, K) are soluble in water and humate with multivalent cations (Ca, Mg, Al) and heavy metals are insoluble.

Fulvic acid

FA is a natural acidic organic polymer that can be extracted from humus found in soil, sediment or aquatic environment. Its name is derived from Latin "fulvus" indicating its

yellow color. This organic matter is soluble in strong acid (pH=1) and has average chemical formula- $C_{135}H_{182}O_{95}N_5S_2$.

Soil Organic Matter

SOM refers to all organic carbon containing substances in soil, ranging from relatively undecomposed plant litters (leaves, stem and roots) and microbial remains to highly polymerized stable product of degradation and synthesis.

Soil Organic Matter (SOM) Pools

	atter (SOM) roots			
Particulars 1.6	A 1:	T 4 - 11 4		
used for	Active	Intermediate	Passive	Recalcitrant
classification				
	Labile/Fresh	Slow/Partial		
Other names	O.M./Plant	O.M.,	Stable/ Humus	-
	residues	Particulate O.M.		
Retention time in soil	Weeks- 1 yr	1 yr-10 yrs	10yrs- 100yrs	100 – 10,000yrs
Size of	of 2mm-0.053 <0.053mm		<0.053mm	< 0.053 mm
molecule	>2 mm	mm (53µm)	(53µm)	(53µm)
Name based on color	Green C	Brown C	Black C	Black C
Oxidation rate	Easily oxidizable	Moderately oxidizable	Non-oxidizable	Non-oxidizable
Accessibility to	Most utilized by	Moderate	Less microbial	Negligible
microbes	microbes	utilization	utilization	utilization
Composition	>2mm sized materials or biomolecules as sugars, starch, SMBC and WSC	<2mm sized composts, debris, particulate OM, manures, crop residues	Mineral associated carbon, humus, humic substances.	Burning crop residues, biochar, charcoal.
Biological activity	High	Moderate	Low	Negligible
C:N ratio	Initially high later gets reduced	Moderate	Moderately high.	High
Roles in soil	Nutrient and CO ₂ release	Soil aggregation, soil structure, air- water ratio, porosity.	Chelation, complexation, pH, CEC, buffering capacity	Soil structure and also CEC, buffering capacity.
Significance of pool	Immediate need of microbes and biological properties improvement.	Physical properties improvement and supply nutrients	Chemical properties improvement. Eg, ion exchange, pH	Long term carbon storage and stabilization.
Management practice to build up the pool	Green manuring, C ₄ crops	Addition of compost, manures, mulches, crop residue management	Fully decomposed compost and manures, vermicompost.	Addition of biochar, ash., partially burnt crop residue.

Glossary of terms

- **1. Humus:** Total of the organic compounds in soil exclusive of undecayed plant and animal tissues, their partial decomposition products and the soil biomass.
- 2. Humic substances: A series of relatively high molecular weight, brown to black colored substances formed by secondary synthesis reactions. This term is used as a generic name to describe the coloured material or its fractions obtained on the basis of solubility characteristics. These materials are distinctive to the soil (or sediment) environment in that they are dissimilar to the biopolymers of microorganisms and higher plant (including lignin).
- **3. Non-humic substances**: Compounds belonging to known classes of biochemistry, such as amino acids, carbohydrates, fats waxes, resins, organic acids etc. Humus probably contains most, if not all, of the biochemical compounds synthesized by living organisms.
- **4. Humification:** the process of fermentation of humic substances; generally, the decomposition of organic material.
- **5. Humic acid:** the dark-coloured organic material which can be extracted from soil by various reagents and which is insoluble in dilute acid.
- **6. Fulvic acid:** The coloured material which remains in solution after removal of humic acid by acidification.
- 7. **Humin:** the alkali insoluble fraction of soil organic matter or humus.
- **8. Hymatomelanic acid:** Alcohol soluble potion of humic acid.

Conclusion

In conclusion, soil colloids are essential components that significantly influence the physical and chemical properties of soils. Their unique characteristics, including size, surface area, surface charges, and zeta potential, play a pivotal role in cation adsorption and the behavior of water within the soil matrix. The colloidal properties, such as cohesion, adhesion, swelling, shrinkage, dispersion, and flocculation, contribute to soil structure and stability. Different types of soil colloids, including layer silicate clays, iron and aluminum oxide clays, amorphous minerals, and organic colloids, collectively enhance the cation exchange capacity (CEC) and anion exchange capacity (AEC) of soils, thereby affecting soil fertility and crop productivity. Understanding the behavior and interactions of soil colloids is crucial for effective soil management practices aimed at improving soil health and optimizing agricultural productivity.