CHAPTER - I

INTRODUCTION

The physical, chemical and biological properties of soils depend to a large extent on the interaction of some Soil Constituents viz. clay minerals, metal ions, oxides and hydrous oxides with the Soil organic matter. It is known that organic and inorganic components of Soil, mainly, humus and clay minerals, do interact. Though considerable amount of work has been done in this field, but due to lack of adequate knowledge on soil organic matter a correct picture of this interaction is still not clear .

Different Scientists[1-5] have made a critical review of the chemical nature of humus. Nearly all of them have concluded that humus is a complex mixture of plant and animal residues in various stages of decomposition. Despite this long history of interest and research[6,7], these materials still defy a precise chemical description because of their inherent complexity and heterogeneity. In recent years the application of sophisticated instrumental methods of analysis to the elucidation of their chemical structure only serves to illustrate the immense complexity and diversity of their constituent units.

The biochemistry of humus formation in Soil has recently been reviewed by Haider *et al.*[8] . It may be added that apart from the humic substances, some of the non-humic constituents in soil are also important in complex formation with clays and other inorganic soil colloids. However such complex formation or interaction is of minor significance. Anyway, of the large number and variety of organic compounds, both simple and polymeric which are known to form complexes with clay minerals[9,9a,10,10a], humic substances are perhaps the most important to the soil scientists.

Demolon and Barbier[11] showed a definite fixation of humic acid and protein by clay. Demolon and Henin[12] studied the relative aggregating powers of humus and clay. Aleksandrova[13] believed that stable clay-humus complexes are formed in the soil with the help of sesquioxides, which make specific bridges between humus substances and the crystal lattice of the clay minerals. These bridges were imagined as complex Fe and Al-humus compounds with non-silicate forms of sesquioxides. They are fixed to the surface of the clay minerals during dehydration by a process of adhesion at the expense of intermolecular types of linkage. Sideri[14] observed that the amount of humus irreversibly adsorbed by clay varies with the character of the clay minerals. He also proposed the idea that the adsorption of humus by clay induces the formation of mixed clay-humus micelles in which the majority of clay particles possess a fairly definite orientation. He[15,16] also concluded that organic matter had been firmly bound to the clay as an anisotropic formation, no marked increase in base exchange capacity should occur. But these studies have not led the author to reach any definite conclusion on the nature of the bonding of clay-humus combination.

Chapek and Sakun[17] thought that most of the humate was held mechanically and only a small fraction was adsorbed by clay, a still lesser amount enters into chemical combination. Mc Henry[18] and Peterson[19] studied the influence of clay minerals on the stability of organo-mineral aggregates and concluded that clay with a high cation exchange capacity gave better aggregation, than those with a low exchange value. Flaig and Beutelspacher[20], using electron microscope were able to demonstrate the presence of polyvalent cations in the system to be necessary for association between humic acid and clays to occur. Among these cations, those of iron and aluminium are particularly effective in promoting adsorption[21,22,23]. It should be recalled, however that Fe^{+3} and Al^{+3} ions are rather special in that they tend to form polyhydroxy complexes at the mineral surface, offering scope for bonding mechanisms other than cation and water-bridge formation to occur. The possibility of anion and ligand exchange reactions to proceed in these systems may explain in the observation that despite the large amounts adsorbed, the affinity of humic and fulvic acids for the clay surface to less than what would be expected on the basis of the polarising power of these cations[24,25]. Khan[26,27], from his studies on the adsorption of organic substances by soil minerals, observed that a portion of the adsorbed humus on clay can not be extracted by alkali treatment. This is due to strong bonding between organic matter and clay mineral. Recently Mortland[28] and Greenland[29] summarised the probable mechanisms of the interaction as described below :

1. Anion Exchange Reactions[29] -

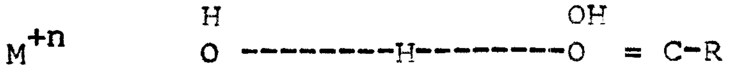
The role of iron and aluminium at the clay surface which readily form polyhydroxy complexes with humic substances have been emphasized. Since Positive sites normally exist on aluminium and iron hydroxides atleast below pH 8.0, organic anions can be associated with these charges by coulombic attraction. The adsorption of the organic anion is readily reversed by exchange with chloride or nitrate. The organic anion can be displaced by raising the pH to 8.0 or 9.0 when the positive charge on the hydroxide is neutralised .

2. Ligand Exchange Reaction[29] -

The anion penetrates the coordination shell of an iron or aluminium atoms in the surface of the hydroxides and becomes incorporated into the surface hydroxyl layer. The anion can not be displaced by leaching with chloride, it is not sensitive to electrolyte concentration but to pH. Adsorption maximum or an inflexion in the adsorption - pH curve occurs at or near the pH, corresponding to the p^K value of the acid species of the anion.

3. Hydrogen bonding[28] -

This is an extremely important bonding process particularly in large molecules or polymers where additive bonds of this type combined with compounds of high molecular weights may produce relatively stable complexes. The proposition considers the formation of 'water-bridges' linking polar organic molecules to exchangeable metal cations through a water molecule in the primary hydration shell in the following manner -



$M^{+n} \quad \overset{H}{O} \text{ --------- } H \text{ --------- } \overset{OH}{O} = C\text{-}R$ where M^{+n} is the metal cation and R-COOH the organic molecules. Greenland[30] also listed the bonding forces that may be operative in clay-humus complexes. He explained the forces involved in the interaction between clays and organic compounds to be, the coulombic attraction between the negatively charged surface and positively charged organic compound or on the otherhand positively charged surface or ion at the surface and the organic anion. According to him Vander Waal's forces may also be operative between the surface and organic compound. The charge induced dipole interactions between the adsorbed molecules of similar species and the other one, the non-polar-dispersion forces between the adsorbed molecules of dissimilar species are the two important types of forces to be considered. When comparatively small known organic molecules are involved, the types and magnitude of the main forces can usually be estimated with a fair degree of accuracy. However, in soils where substances of widely varying sizes are subject to adsorption and where the exact nature of the reacting substances is largely unknown, an accurate analysis or estimation of the magnitude of the various forces involved is almost impossible .

The above discussion on the principles of the interaction between organic compounds and clay minerals serves to emphasize the complexities involved and the deficiencies of our knowledge. So in consideration of interactions of clay and humus in soils, it is obvious that one gets confused because of the following reasons: (a) One is to deal not with a single mineral but with mixtures including transformed minerals that are not always clearly defined. (b) The organic compounds include everything from recently added undecomposed plant and animal substances to thoroughly decomposed materials like humus. (c) The conditions in soils, unlike those in the laboratory never remain constant.

The changes in environmental conditions are attributed chiefly to variations in weather, but those brought about by man through cultivation, addition of fertilizers, liming and cropping are often to be seriously taken in view. All these natural and man-made variations affect the nature of both clay and the soil organic matter as also the interaction products. Alexandrova[31] refers to the organic-mineral colloids as a complex of highly dispersed clay minerals, humic substances and organo-mineral compounds in a state of alliance. The soil organic matter in a broad sense consists of non-humic and humic substances. The non-humic substances may include at least traces of almost any compound that normally occurs in plant and animal tissues and their biological non-gaseous decomposition products. The humified matter can be separated into four groups.

1) Humin - Insoluble in alkali .

2) Humic acid-soluble in dilute alkalies and precipitated by acids.

3) Fulvic acid - Soluble in alkalies and not precipitated by acids.

4) Hymatomelanic acid - Soluble in alkalies and precipitated by acids, the precipitate is soluble in alcohol .

Some workers[30,32] have attempted to determine the percentage of the total soil organic matter that is adsorbed on the mineral portion of the soils. These investigations are greatly handicapped due to lack of a method that will bring about a clear cut separation of the free organic matter from the adsorbed complexed material. Some of the mechanism discussed earlier, points to the formation of complexes that are so stable that it is impossible to break chemical bond without partially destroying the organic portion of the complex. On the other hand, some of the bonds are so weak that there is considerable doubt as to whether there is a real complex or only an organo-inorganic mixture. According to Greenland[30] the more thoroughly decomposed is the organic matter, the greater will be the tendency to form complexes with the clays. Most of this organic matter exists in the colloidal fraction of the soil but larger soil particles have organic coatings.

In addition to other contributions, the importance of clay-organic matter interactions which assist the formation of aggregates thereby rendering a soil of greater porosity and hence help the free movement of water in the soil should be taken into consideration. This clay-humus complex undoubtedly plays an important role in plant nutrition. The presence of humus in soil modifies the properties of the latter in such a way that it becomes a more favourable and more balanced medium for plant growth. Its presence modifies the physical properties of soil such as colour, texture, structure, moisture holding capacity and aeration[33,33a]. Chemically, humus modifies the nature of the soil by influencing the solubility of certain soil minerals, forming compounds with some elements, such as iron, aluminium, molybdenium etc., which render them more easily available for plant growth, and finally increasing the buffer properties of the soil[34]. Humus also favours the nutrition of plants by serving as a source of energy for the development of microorganisms which ultimately makes the soil a better medium for the growth of higher plants[35]. The activities of microorganisms in soils are influenced both indirectly and directly by the interaction of organic matter with clays. The indirect effects, which are usually beneficial, are exerted chiefly through the improvement in physical condition of the soil. Better aeration and water-retention favour the activities of the more beneficial microorganisms and repress anaerobes. Among the direct effects may be listed the adsorption of (i) the substrate (ii) the bacteria or their released enzymes (iii) the metabolic or decomposition products of microorganisms and (iv) organic substances added to the soil .

The presence of humic acids in soil controls the uptake of nutrients e.g. K^{+1}, Ca^{+2}, Fe^{+3}, Al^{+3} etc., by plants. Natural chelates present in soil hook-up the plant food and make them available to plants. The uptake of micronutrients by plants from different soils is related to humic acid chelators. The complexing property of humic acids with clay is of great value in increasing the availability of phosphate fertilizers and certain trace elements which are rendered insoluble in the soil by fixation mechanisms[36]. Organic matter also counteracts the activity of certain toxic substances in the soil by complex formation. The accumulation of insecticides, fungicides, herbicides and other kinds of pesticides are harmful to plant growth and the adverse effects of such pesticides can be overcome by mixing the soil with good quantity of humus substances having high cation exchange capacity[37]. Sometimes favourable actions may be achieved due to chelations by humus substances with metals e.g. Pb, Cu, Hg, Zn, which are usually considered as pollutants.

In the three phase system, i.e. solid-liquid-gas which constitutes a soil, the liquid phase is the phase that directly feeds the plant. Not only is the solvent water a necessity of plant life, the liquid phase is also the medium of transport for the plant nutrients and to a certain extent, of the gases involved in the metabolism of the plant. Clay-humus complex formation influences this three phase system perhaps to the maximum extent through direct and indirect avenues.

REFERENCES (CHAPTER - I)

1. Sprengel, C. - Kastners Arch. Ges. Naturlehre, 8, 145 (1826).

2. Berzelius, J. - 'Lehrbuch der chemie' : Dresden (1839).

3. Braconnot, H. - Ann. Chemie., 61, 187 (1807).

4. Mulder, G.J. - J. Prakt. Chem., 32, 321 (1844).

5. Baumann, A. - Mitt. K. Bayr. Moorkult., 3, 52 (1908).

6. Kononova, M.M. - Soil organic matter : Pergamon Press, Oxford (1966).

7. Schnitzer, M. and Khan, S.U. - 'Humic Substances in the Environment', Marcel Dekkar, N.Y. (1972).

8. Haider, K., Martin, J.P. and Filip, Z. - 'Humus Biochemistry' - In E.A. Paul and A.D. Mclaren (Editors). Soil Biochemistry- Vol. 3, Marcel Dekkar, N.Y. (1975).

9. Greenland, D.J. - Interaction between clays and org. compounds in soils -
    (i) Mechanism of interaction between clays and defined organic compounds - soils and fertilizers, 28 : 415-425 (1965).
    (ii) Adsorption of soil organic compounds and its effect on soil properties - soils and fertilizers, 28 : 521-532 (1965).

9. (a) Mortland, M.M. - clayorganic complexes and interactions . Advances in Agronomy, 22 : 75-117 (1970).

10. Theng, B.K.G. - Formation Properties and Practical application of clay-organic complexes - Journal of the Royal Society of Newzealand 2, 437-457 (1972).

10. (a) Theng, B.K.G. - The chemistry of clay-organic reactions, Adam Hilger Ltd., London (1974).

11. Demolon, A. and Barbier, G. - Compt. rend, 188, 654 (1929).

12. Demolon, A. and Henin, S. - Soil Res. 3, 1 (1932).

13. Aleksandrova, L.N. - 'Problems of soil science', IZd. Akad. Nauk, USSR (1962) .

14. Sideri, D.I. - Soil Sci., 42, 461 (1936).

15. Sideri, D.I. - Soil Sci., 46, 129 (1938).

16. Sideri, D.I. - Soil Sci., 46, 267 (1938).

17. Chapek, M.V. and Sakun, N. - Kolloid-Ztschr., 107, 41 (1944).

18. Mc Henry, J.R. - Iowa, Sta., Coll. J. Sci., 20, 25 (1945).

19. Peterson, J.B. - Soil Sci., 61, 247 (1946).

20. Flaig, W. and Beutelspacher, H. - Z. Pfl Ernahr. Dung, Bodenk, 52, 1, (1951).

21. Martin, A.E. and Reeve, R. - Soil Sci. 11, 369 (1960).

22. (a) Sen, B.C. - J. Indian Chem. Soc. 37, 793 (1960)
    (b) Sen, B.C. - J. Indian Chem. Soc. 41, 145 (1964)

23. Kobo, K. and Fujisawa, T. - Soil Sci. and Plant nutrition (Tokyo), 9, 36, (1963).

24. Theng, B.K.G. and Scharpenseel, H.W. - Proceedings of the International Clay Conference, Mexico city, 643 (1975).

25. Theng, B.K.G. - Geoderma, 15, 243 (1976).

26. Khan, D.V. - Pedology, USSR, 637 (1950).

27. Khan, D.V. - Doklady Akad. Nauk, USSR, 81, 461 (1951).

28. Mortland, M.M. - Adv. Argon, 22, 75 (1970).

29. Greenland, D.J. - Soil Sci. 111, 34 (1971).

30. Greenland, D.J. - Soils Fertil, 28, 415 (1965)

31. Alexandrova, L.N. - Trans. Int. Congr. Soil Sci. 7th Madison, Wisc. Comm. II - 74-81 (1960).

32. Mortland, M.M. and Wolcott, A.R. - Soil Nitrogen, Agronomy, 10, 150-197 (1965).

33. Waksman, S.A. - "Humus", Origin, Chem. Comp. and Importance in Nature

33. (a) Review of Soil Research in India, Part-II 12th International Congress of Soil Science, New Delhi, India, Feb. 1982 .

34. Even-Haim, A. - 'The use of isotopes in soil organic matter studies' - Pergamon, N.Y. 3-9, and 49-59 (1966).

35. Lavesque, M. - Can. Jr. Soil Sci. 50, 385 (1970) .

36. Hazra, G. - D. Phil. Thesis, C.U. (1974).

37. Gaur, A.C. - Science Reporter, 7, 421 (1970).