ION EXCHANGE PHENOMENON IN SOILS OF THE UAR

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DISSERTATION

Submitted in Partial Satisfaction of the Requirements for the Degree
Of

DOCTOR OF PHILOSOPHY

in

SOIL SCIENCE

Soils Department
Faculty of Agriculture
Ain Shams University

1975

APPROVAL SHEET

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Title : Ion Exchange Phenomenon in Soils of U.A.R.

Submitted for The Degree
of
DOCTOR OF PHILOSOPHY
in
Soil Science

This Dissertation has been
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Date: / /1975


جامعة عين شمس
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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Hassan Hamdi, former dean of Faculty of Agriculture, Ain Shams University, Dr. Adel El-Leboudi, Associate Professor of Soil Science and Plant Nutrition, Department of Soils, Faculty of Agriculture, Ain Shams University, for suggesting the problem, supervision, sincere guidance and interest during the course of study and writting the dissertation.

The author also like to extend his deep appreciation to Dr. Saad El-Demerdash of the Desert Institute for introducing certain facilities through the course of investigation.

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1. INTRODUCTION

One of the most important features of soil is its capacity to sorb or bind ions reversibly. As most of the chemical reactions that determine the characteristics of a natural soil body or alter the properties of fertile soils are related to ion exchange reaction its evaluation is of paramount importance in studies dealing with physical, chemical and biological features of soil.

Since exchange materials in the soil often have greater adsorption capacity for cations than for anions, exchange studies have been mostly confined to the exchange reactions of cations.

In Egyption soils, developed under different conditions, there is a broad variations in the exchangeable cations from normal soils to calcareous and to salt-affected ones. These ion species are expected to exert specific influence on the mineral-bound ions, when they constitute integrating part of their lattices; examples are like K^+ in mica as well as illite and K-feldspars, Mg^{2+} in montmorillonite and vermicultive, Ca^{2+} in calcite and Ca-feldspars and Na^+ in Na-feldspars. Hence, the presence of these ions in an exchangeable form and/or in the soil solution is likely to stabilize these minerals, while their absence may enhance the weathering of, or the isomorphic substitution in minerals having other ion species as lattice constituents.

The aim of the present study is to shed light on the nature of adsorption-desorption patterns of the most common cations on alluvial soils, and to investigate the role of important factors involved in such phenomenon.

2. REVIEW OF LITERATURE

Since the early discovery of Way (1950) regarding ion exchange reactions in soil systems, a great attention is directed towards the study of such phenomenon due to its pronounced effect on soil properties. These studies are reported in comprehensive review given by Kelley (1948). From such studies, ion exchange is considered as the most important of all processes occurring in soil, as this property is intimately connected with a large number of chemical properties such as weathering of minerals, nutrient status and absorption by plants, swelling and shrinkage of clays, and leaching of salts. The property is defined as a reversible process by which cations and anions are exchanged between solid and liquid phases, and between solid phases if in close contact with each other. For cation exchange is the more to our concern, it is convenient to review the aspects related to such property in the following.

2.1. Origin of Cation Exchange Phenomena in Soil.

Previous investigators have shown clearly that cation exchange property of a soil is almost entirely related to the colloidal materials of the soil, i.e., clay, silt, amorphous inorganic materials and organic matter.

Considering the CEC of the clay minerals, Grim (1953) pointed out that the broken bonds around the edges of the silica-alumina units, substitution within the lattice structure as well as the hydrogen of exposed hydroxyls are the main causes of such property. In this accordance, Bolt(1955) was of the opinion that the charge of clay particles result partly from substitution of alumino-silicate lattice and partly from the existence of proton transfer mechanism on the edges of clay particles. This surface charges are balanced by attracting cations and by repelling anions during ion exchange process, Helmy (1963).

According to Marshall (1964), exchange was found to involve at least two functions, one involved the fixed charge on the lattice frame work; ions held in this way gave a pH-independent CEC. Whereas, the second involved the pH-dependent function located at the edges of clay particles. The second function appears to arise from isomorphous substitutional charge (permanent negative charge) working by hydroxy-Al, charged positively by edge-Al $(OH)_2$ groups, and restored by deprotonation of the latter on addition of base, De Villiers and Jackson (1967). Marshall (1964) pointed out that this function is responsible for the main part of the capacity for kaolinitic clays whereas it was of small magnitude in the montmorillonitic ones.

These distinctions were also clearly exprssed by Schofield (1939) and have been developed further by Fieldes and Schofield (1960). In agreement with the aforementioned ideas, Lefebvra and Merlaux (1963) showed evidence that the exchange capacity of leached soils was due to both permanent charges and variable charges that varied with the pH; they ascribed the variable charges, when much large, to the high organic content. The pH-dependent CEC was also mentioned by Ulrich (1966), Mocik (1967) and Devilliers and Jackson (1967). The latter authors had rendered the pH-dependent negative charge to the presence of pedogenically formed aluminous chlorite. They further added that part of the initially blocked iscmorphous substitutional negative charge of the layer structure is released by deprotonation of $Al(OH)_2$ groups of the positively charged hydroxy-alumina upon addition of base.

The pH-dependent CEC of many soils constitutes a major portion of the total exchange acidity. A recent comprehensive review of the subject by Coleman and Thomas (1967) indicates that pH-dependent CEC has two components: 1) weakly dissociated acid groups of soil organic matter and 2) sesquioxide coatings on clay mineral surfaces or partially neutralized complexes of Al and Fe ions in the interlayers of 2:1 layer silicates. However, separation of the total pH-dependent CEC into these two components is less certain.

Pratt and Bair (1962) measured the CEC of a number of California soils at different pH values, and found that the pH-dependent CEC was related to both organic matter and clay. Similarly, Helling et al. (1964), using multiple regression analysis of various soil characteristics indicating CEC at different pH values, showed that CEC of both clay and organic matter increased linearly with pH. Direct measurements of the contribution of organic matter of pH-dependent CEC have been attempted by McLean et al. (1965) and Bhumbla and McLean (1965) who found that the increase in CEC from pH 7.0 to pH 8.2 was directly correlated with the organic matter content; the removal of organic matter decreased the CEC at pH 8.2 by 1.5 meq/100 g for each gram of organic matter. They also observed that the reaction of these soils with KCl removed Al and decreased pH-dependent CEC. This led them to conclude that pH-dependent CEC is related to hydroxy Al ions in addition to organic matter. In a subsquent study, McLean et al. (1965) reported that the increase in CEC at higher pH resulted from the activation of weak acid-exchange sites on organic matter that were initially occupied by Al. Investigations carried out by Turner and Nicol (1962), Schnitzer and Gupta (1964), and Martin and Reeve (1960) pointed out that Fe and Al complexes with organic matter exhibit weak acid characteristics and could thus contribute to pH-dependent CEC. Although the conclusion of McLean _et al._ (1965) that the exchange sites activated at high pH were initially occupied by Al may be correct, Al removed by NH_4OAc at pH 4.8 may also include salt exchangeable Al as well as Al from amorphous oxides in soils.

Studies on the contribution of Al and Fe interlayers or coatings to the pH-dependent CEC have been limited to minerals treated with partially neutralized Fe or Al salt solutions. A number of reports cited by Sawhney (1960), Coleman and Thomas (1964), and Hsu and Bates (1964) show that neutral salt CEC of montmorillonite and vermiculite decreases after treatment with partially neutralized Al or Fe salt solutions. Sawhney (1968) has further demonstrated that in vermiculite, treatment with un-neutralized Al salt solution also reduced CEC. As the CEC determined with neutral salts decreases, the pH-dependent CEC increases as indicated by titration curves of layer silicates treated with partially neutralized Al and Fe salt solutions.

Turner and Nicol (1962), Coleman and Thomas (1964), and Helling et al. (1964) illustrate pronounced buffer capacity in the pH range of 5 to 8. These buffer capacities have been assumed to correspond to the pH-dependent CEC; fairly good agreement between buffer capacity and pH-dependent CEC was obtained in some cases, Coleman and Thomas (1964). Determination of the contribution of interlayers to pH-dependent CEC of soil clays from their titration curves is uncertain because organic matter in clays marks the inflection points, Volk and Jackson (1963).

The foregoing authors clearly show that the contributions of organic matter and sesquioxide coatings or interlayers to the pH-dependent charge in soils have not been determined successfully thus far. The two, however, are shown to be differentiable as follows: since sesquioxide interlayers or coatings are believed to precipitate as hydroxides at alkaline pH and release exchange sites, any increase due to their precipitation should be permanent. On the other hand, an increase in CEC by the release of protons from weakly dissociated organic groups should be reversible. Thus, the reversible portion of the CEC determined at high pH may be attributed to organic matter and the irreversible portion to Al or Fe interlayers and coatings.