ADSORPTION OF SOME MICRONUTRIENTS ON CLAY MINERALS AND SOILS

by

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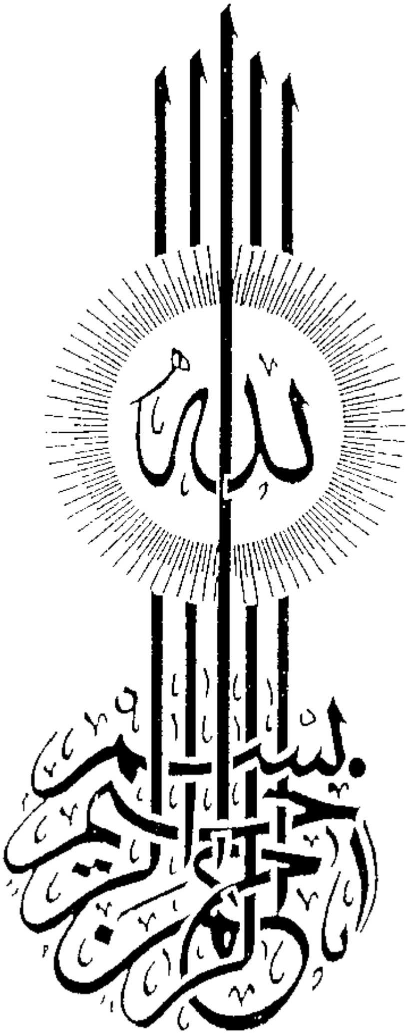
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1. INTRODUCTION

The term "micronutrient (Iron, manganese, zinc, Copper, boron and molybdenum) has been coming into use to signify plant nutrients that are essential to plants but are needed only in very small amounts.

It was found that copper and zinc deficiency usually occurs in sandy and calcareous soils of Egypt. For this reason both copper and zinc has been chosen as the object of the present investigation.

Application of soluble copper and zinc to soils, either alone or in conjunction with other compounds, as insecticides, pesticides and fungicides as well as trace elements, fertilizers has become more common. It is well known that the availability of these nutrients to plants is governed by adsorption reactions.

Moreover, the studies of copper and zinc solubility in soils are in agreement with the general tendency of these nutrients to form a number of compounds of low solubility. Their precipitation as hydroxide, carbonate or phosphate could reduce their soluble form in soils to low levels but the few data available indicate that such reactions do not satisfactorily account for the extremenly low concentrations required to induce their deficiency. Recent information indicate that adsorption reactions could reduce copper and zinc solubility to deficiency levels. Such adsorption reactions may occur on many types of surfaces including clay minerals, lime minerals and organic matter.

The object of this work is to determine the adsorption rate of copper and zinc on clay minerals and soils as influenced by time of reaction, pH of the media, kind of nutrient salt used as well as its concentration. In addition, the release of pre - retained copper and/or zinc from clay minerals and soils was also studied in order to throw some light on the nature of their adsorption and to find out whether adsorption processes are subjected to side reactions which may lead to either permanent fixation or release.

Cu^{++} retention, whilist the conversion of H - soils to Ca - soils showed a higher Cu^{++} - retention than the original soil. Besides, agreate portion of the Cu^{++} retained by these samples existed in the exchangeable forms in comparison to organic soils.

Studies of Lal et al (1971) showed rather high copper fixation by soils from $CuSO_4$, the fixation being higher in loam than in silty loam.

Mclaren and Crawford, (1973) showed that the adsorption of copper by soils and soil constituents conform to the Langmuir equation. The investigated soils were found to have specific adsorption maxima at pH 5.5 of 340 and 780 ug^{-1}. They also found that adsorption maxima for soil constituents were in the following order manganese oxides > organic matter > iron oxides > clay mineral.

2.1.2. Adsorption of Copper by some clay minerals :-

Antipov - Karataef, (1947 a) noted that Cu^{++} is retained by soils and clays in two forms :- exchangeable and chemosorbed. Montmorillomite clays and soils high in organic matter tie up Cu^{++} much more rigidly than Ca^{++} and Mg^{++}. However in the case of montmorillonitic clays the rigidity of adsorption is reversed.

Menzel and jackson (1949) studied the sorption of Cu^{++} by potassium saturated montmorillonite and kaolinite, and mentioned that, the simple exchange of cupric ion for potassium ion sorbed on the minerals occurred only in acid diluted copper solution. The H^{+} ions released from hydroxy cupric ions which are buffered, to a limited extent, by AL^{+++} dissolved from the clays, The hydroxy cupric ions sorbed were shown by the release of less K^{+} than Cu^{++} sorbed accompanied by a pH decrease. Their data showed that more meq. of copper were sorbed by the clay than the amounts of potassium released by a mechanism of lattice building on the clay crystal.

De Mumbrum and jackson (1956 b) using infra-red technique indicated that the mechanism of copper exchange reaction with layer silicate clays is through replacement of hydrogen from the structural OH^{+} groups of the clay by copper. Their evidence was advocated by treating montmorillonite with copper which resulted in a decrease amounted to 2.8 μ hydroxyl intensity (amounting to 25 %) relative to Ca^{++}, K^{+} and H - clays used as standard proving areaction with octahedral OH^{-} in the layer silicates.

Mitra et al (1955) investigated the exchange reactions of Cu^{++}, Ca^{++}, K^{+}, and H^{+} ions with various clay minerals in acid systems. They found that copper adsorption from Cu SO_4 solutions was much greater by montmorillonite than by kaolinite. Muscovite and biotite adsorbed very little Cu^{++}. The release of Ca^{++} ions was found to exceed that of Cu^{++} adsorbed by an amount equal to the H^+ adsorbed. The amount of Cu^{++} adsorbed by K - clays exoeeded the K^+ released, indcating the probable uptake of $(Cu\ OH)^+$.

Ringwood (1955), Heydemann (1959) and Richardson and Hawkes (1958) mentioned that Cu^{++} is the most strongly bound cation to clay minerals and silicate mineral surfaces according to the Freundlich adsorption isotherm, where as in calcite a chemical reaction took place.

Studies of Konlev <u>et al</u> (1962) revealed that the adsorption energy of the metal ions with bentonite were as follows : $Ag^+ > pb^{++} > Ni^{++} > Cu^{++}$. The exchange constants for Ni^{++} and Cu^{++} varied owing to the heterodynamic nature of the adsorption sites in the bentonite as well as to hydrolysis of the salts. The equilibrium constants for Ag^+, Ni^{++}, Cu^{++} and pb^{++} decreased with decreasing ionic strength of the solutions.

2.1.3 Adsorption of zinc by soils :-

Zinc has been recognized as a trace constituent of various minerals in soil. Powers and Pange(1947) and Mitchell (1955) reported that zinc occurs in ferromagnesium minerals, chiefly pyroxens and magnetite in basic rocks, and biotite in acid rocks.

Jones et al (1936), Hibbard (1940), Brown (1950) and Nair et al (1959) reported that zinc is known to exist in the soil in three forms, water soluble, replaceable and non-replaceable. Soils vary widely in their zinc supplying regardless of the amount of zinc present in non-replaceable form. They also found that some of the available zinc is undoubtedly held as cation on the exchange materials, both clay and organic material in soils.

Wright et al (1955) and Throne (1957) demonstrated that the adsorption reactions could reduce zinc solubility to the level of deficiency. Such adsorption reaction can occur on many types of surfaces including clay minerals, organic matter colloides and lime minerals, the strongest adsorption of zinc takes place on surface of high magnesium saturated. They also stated that zinc solubility in soils stands in agreement with the general tendency of this element to form a number of compounds of low