

II. CHEMISTRY

Soil Chemistry

SPECIFIC ADSORPTION OF COPPER AND ZINC IN DIFFERENT SOILS

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Specific adsorption of copper and zinc in four different soils viz., Peaty and Red soils of Kerala and Red Alluvial soils of U.P. was studied by equilibrating the soil with different concentrations of copper and zinc. It was found to vary in different soils. The specific adsorption isotherms showed that alluvial soils exhibited more adsorption and peaty soils the least and it was found to increase with an increase in pH and manganese oxide contents. Hydrogen saturation of all soils resulted in a reduction in specific adsorption of copper and zinc in all the soils but calcium saturation of soils slightly increased the adsorption of copper but reduced that of zinc as compared to original soils. The Langmuir constants, specific adsorption maximum and bonding term worked out for original soils were also more in alluvial soils and less in red soils of Kerala and followed a direct relationship with pH. The calculated non-specific adsorption capacity showed a different trend and showed maximum value for peaty soils and minimum for alluvial soils and it tended to decrease with an increase in pH.

Key words: Adsorption isotherm; Exchange; Selectivity coefficient; Illite; Nickel chloride.

INTRODUCTION

MICRONUTRIENT cations of copper, zinc, manganese and iron may be adsorbed by soil colloids in amounts in excess of their conventional cation exchange capacities. In addition to cation exchange mechanisms, these micronutrients enter into specific adsorption processes through covalent bonding to certain functional groups on colloidal surfaces. Adsorption of micronutrient cations by these colloids can take place in the presence of amounts of calcium and other major nutrient cations large enough to prevent adsorption on normal cation exchange sites (McLaren & Crawford, 1973). This phenomenon of adsorption of applied micronutrient cations by soil has been termed as specific adsorption. This is exhibited by all the major types of soil colloids that is by clay minerals (Tiller, 1968), organic matter (De Mumbum & Jackson, 1956) and free oxide (Mckenzie, 1967). Any variation

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in the aforesaid soil constituents may greatly affect the degree of adsorption in different soils. Since an equilibrium always exists between various forms of micro-nutrients, this type of adsorption reaction may greatly affect their availability.

MATERIALS AND METHODS

Four Indian soils viz., Peaty and Red soils of Kerala and Red and Alluvial soils of U.P. were used for the present study. The soils collected were air dried, powdered, passed through 100 mesh sieve and oven dried. From the original soils two artificial soils were prepared by treating HCl and CaCl₂ and resulting samples were designated as H-soil and Ca-soil. Hydrogen soils (H-soils) were prepared by shaking the soils with 0.1N HCl (1 : 10 soil : acid) for one hour and then keeping overnight. Next day, it was filtered through a Buchner funnel with suction and further leaching with the acid solution. The soil was washed free of chloride ions with distilled water and finally with alcohol. Calcium soils (Ca-soils) were prepared from H-soils by treating it with 1N CaCl₂ (1 : 10 soil : solution) for red and alluvial soils and 2N CaCl₂ for peaty soils. Original as well as prepared H- and Ca-soil were analysed for pH, organic matter, Fe, Mn and Al oxides (Table I) Oxides of Fe, Mn and Al were extracted by dithionite method (Dewis & Freitas, 1970) and iron in the extract was determined colorimetrically by orthophenanthroline method, manganese by periodate method (Jackson, 1967) and aluminium by aluminon method (Dewis & Freitas, 1970).

TABLE I
Some characteristics of the soils

Sl. No.	Soil	pH	Organic matter (%)	Free Fe (%)	Free Mn (ppm)	Free Al (%)
1	PS (O-S)	3.3	6.97	0.310	138.90	0.063
2	PS (H-S)	3.1	6.56	0.330	111.12	0.048
3	PS (Ca-S)	4.6	6.46	0.330	83.34	0.021
4	RS (K) (O-S)	5.1	0.87	0.036	166.68	0.016
5	RS (K) (H-S)	3.7	0.82	0.036	111.12	0.023
6	RS (K) (Ca-S)	4.8	0.79	0.036	83.34	0.011
7	RS (UP) (O-S)	6.1	0.89	0.054	361.14	0.009
8	RS (UP) (H-S)	4.8	0.88	0.063	194.46	0.014
9	RS (UP) (Ca-S)	5.2	0.88	0.063	138.90	0.007
10	AS (O-S)	7.3	0.70	0.036	280.02	0.011
11	AS (H-S)	4.6	0.67	0.071	194.46	0.016
12	AS (Ca-S)	5.6	0.66	0.054	138.90	0.013

PS = Peaty Soil, RS (K) = Red Soil of Kerala, RS (UP) = Red Soil of U.P., AS = Alluvial Soil.
O-S = Original Soil, H-S = Hydrogen Soil, Ca-S = Calcium Soil.

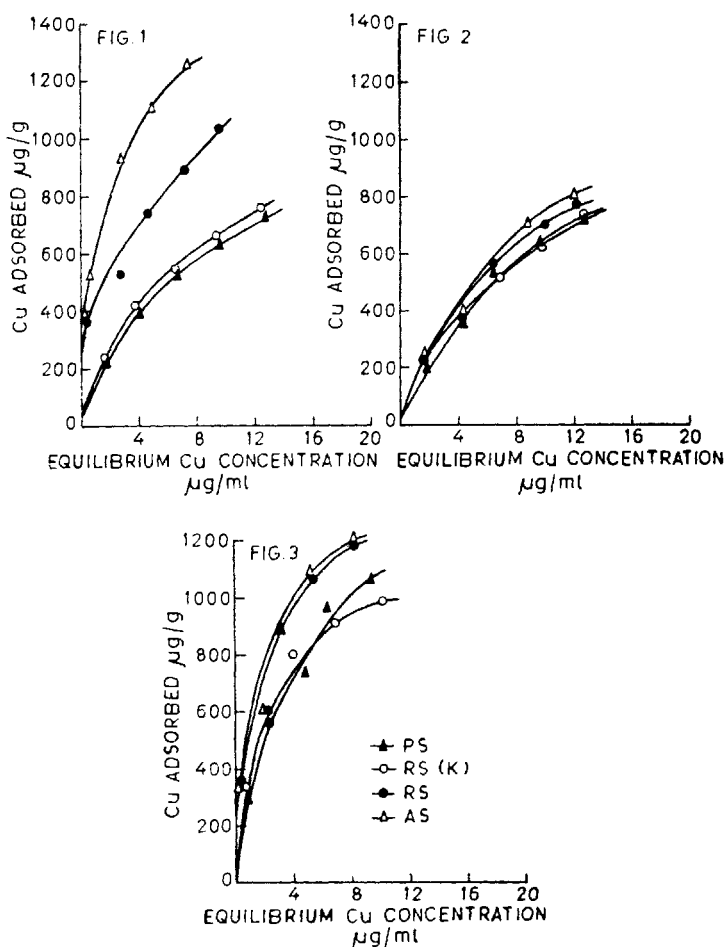
Measurement of Specific Adsorption

Specific adsorption of copper and zinc in original and artificial soils was studied by adding solution of copper sulphate and zinc sulphate respectively in the

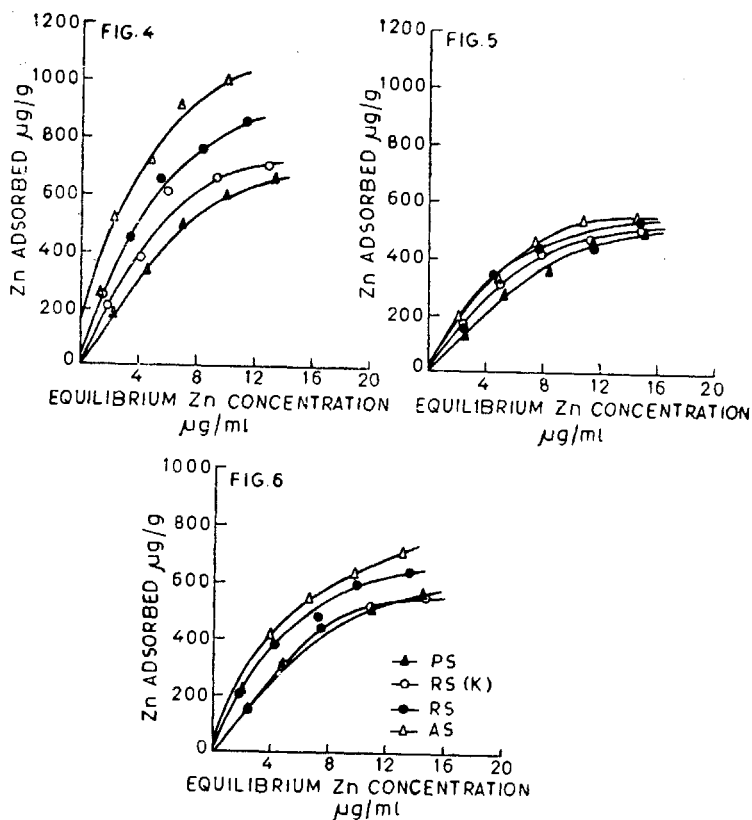
range of 0 to 20 $\mu\text{g}/\text{ml}$. The results were plotted as adsorption isotherms. In order to minimise non-specific adsorption, it was measured in the presence of 0.05 m CaCl_2 .

One gram sample of soils were equilibrated with a series of 100 ml solutions containing 0.05 M CaCl_2 and 0, 4, 8, 12, 16 and 20 μg Cu or Zn/ml. Six hours shaking followed by standing overnight was adopted in all the cases for attaining equilibrium. The samples were then centrifuged and the supernatant liquid analysed for copper and zinc. Copper or zinc adsorbed was calculated from the initial and final concentration of copper or zinc in the solution. Adsorption isotherms were determined at room temperature.

From these values adsorption isotherms were plotted for all the soil keeping equilibrium copper or zinc concentration ($\mu\text{g}/\text{ml}$) on the X-axis and copper or



Figs. 1-3. Adsorption isotherms of copper for different soils. 1. Specific adsorption of copper by original soil. 2. Specific adsorption of copper by H-soil. 3. Specific adsorption of copper by Ca-soil.



Figs. 4-6. Adsorption isotherms of zinc for different soils. 4. Specific adsorption of zinc by original soil. 5. Specific adsorption of zinc by H soil. 6. Specific adsorption of zinc by Ca-soil.

zinc adsorption ($\mu\text{g/g}$) on Y-axis and are presented in Figs. 1-3 and 4-6. Specific adsorption maxima (a) Langmuir bonding term (b) were calculated by adopting the form of equation used by McLaren and Crawford (1973). The form of the equation used was :

$$\frac{C}{x} = \frac{1}{ab} + \frac{C}{a},$$

where,

x = the amount of copper or zinc adsorbed by unit weight of soil ($\mu\text{g/g}$).

C = equilibrium copper or zinc concentration in solution ($\mu\text{g/ml}$).

a = Langmuir adsorption maximum ($\mu\text{g/g}$).

b = Langmuir bonding term ($\text{ml}/\mu\text{g}$).

Non-specific adsorption capacity for copper and zinc was calculated from the CEC values determined by the method of Bascomb (1964).

RESULTS AND DISCUSSION

Some of the characteristic studied for original, H- and Ca-soils are presented in Table I. The specific adsorption isotherms of copper and zinc are presented in Figs. 1 to 3 and 4 to 6. The ability of the soils to adsorb copper and zinc varied markedly. There was a great variation in the adsorption of copper and zinc by original soils as compared to H- and Ca-soils. Original soils adsorbed higher amounts of copper and zinc within a wide range. The highest adsorption was noticed in alluvial soils and the lowest in peaty soils and it was found to be very much dependent on pH , decreasing with an increase in acidity of the soil. This may be due to the formation of more hydrolysed species of copper ($Cu OH^+$) and zinc ($Zn OH^+$) at pH levels near and above 7.0 which may be easily adsorbed or precipitated. Similar type of adsorption of copper and zinc was reported by DeMumbrum and Jackson (1956), Bingham *et al.* (1964) and Mishra and Tiwari (1966). Hydrogen saturation of the soils resulted in a reduction in the adsorption of copper and zinc in all the soils and calcium saturation slightly increased the adsorption of copper but reduced that of zinc when compared to original soils. Reduction in adsorption of copper and in H-soils of zinc by both hydrogen and calcium saturation may be attributed to the antagonistic effect of H^+ and Ca^{++} ions which prevent the entry of Cu^{++} and Zn^{++} ions into the adsorption sites. Also hydrogen leaching may result in the loss of carbonates. However, calcium saturation increased the adsorption of copper by soils. DeMumbrum and Jackson (1956) also observed that Ca-montmorillonite and Ca-peat could accumulate Zn or Cu from very dilute neutral solutions either in presence or absence of excess Ca^{++} ions.

Specific Adsorption Maximum (a)

The data obtained on the adsorption isotherms were plotted in accordance with the Langmuir adsorption equation. It was found that though they produced more or less linear graphs, the artificial soils, particularly in the case of copper, did not follow the Langmuir adsorption equation well. Hence the Langmuir constants were determined in the case of original soils only (Table II). Specific adsorption maximum (a) for copper and zinc was highest for alluvial soils and lowest for red soils of Kerala and was found to be very much dependent on pH . Though organic matter is very important in adsorption reactions, its effect was masked by the pH of the soil. But it was found to increase with an increase in the manganese oxide content of the soil which suggests that it is an important factor which controls the adsorption of copper and zinc.

Bonding Term (b)

Examination of bonding term for different soils (i.e., the ratio of the specific rate constants for adsorption and desorption) reveals that the soils varied in the mean strength with which they could adsorb Cu or Zn. The bonding energy tended to increase with increasing pH and showed the maximum value for alluvial soils. The lowest value was noted for peaty soils.

TABLE II

Langmuir constants for specific sorption of copper and zinc by different soils and calculated non-specific sorption capacities

Sl. No.	Soil	Specific Adsorption Maximum (a) (μ/g)	Bonding term (b) (ml/ μg)	Non-specific adsorption ($\mu g/g$)
<i>copper</i>				
1	PS	1180.64	0.125	8139.47
2	RS (K)	1169.59	0.143	3825.11
3	RS (UP)	1228.50	0.406	4066.56
4	AS	1303.78	1.667	3609.07
<i>zinc</i>				
5	PS	1414.43	0.070	8375.18
6	RS (K)	1183.43	0.128	3935.88
7	RS (UP)	1483.68	0.126	4184.32
8	AS	1956.95	0.134	3713.58

Nonspecific Adsorption

The non-specific adsorption calculated on the basis of CEC values far exceeded the specific adsorption maximum (Table II) showing a different trend. The non-specific adsorption was highest in the case of peaty soils and lowest in the case of alluvial soils. But specific adsorption followed a different pattern. Which reveals that specific adsorption is not dependent on the cation exchange sites but mainly on the colloidal surfaces like organic matter, manganese oxides etc., as suggested by McLaren and Crawford (1973).

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