

Studies on the chemistry of phosphorus compounds in the calcareous soils treated with organic materials

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previous studies showed fairly sometimes contradictory informations involving phosphorus compounds that calcareous soils. little and perhaps about the reactions may take place in. To elucidate the nature of such reactions, CaCO_3 (chemical compound), fractionated oleitic limestone and atypical calcareous soil were investigated for their reactivity with P either from phytic acid or hydroxyapatite in presence of humic acids derived from three organic raw materials. The recovery and characterizations of humic acids including elementary analysis, infra-red and ultra-violet spectroscopy were carried out. The ability of humic acids for P solubilization was compared using H_2O , NaHCO_3 and NaOH as P solvents. Langmuir, Freundlich And Van-Huay equations were tested for their reliability to assess P adsorption relations in the systems including; different limestone fractions, three different humic acids and (calcareous soil + humic acid). The results obtained are summarized as follows:

a) Recovery and characterization of humic acids. Recovery of humic acids dominated than fulvic acid and that seems to be dependent on the total organic carbon content of organic materials and their rate of decomposition. The highest and lowest values of total N content of humic acids were obtained from humic acids derived from peanut and barley straw, respectively. The aromatization of humic acid prepared from barley straw exceeded those originated from other sources. The infra-red test showed that, the greatest intensity of humic acids at 3400 cm^{-1} was obtained in humic acid derived from barley straw, compared with other sources. The highest humic acid O/H ratios were the greatest O-H stretch absorption at 3400 cm^{-1} , at 1400 cm^{-1} , at 1200 cm^{-1} and at 1128 cm^{-1} when they were treated with KH_2P_4 . As the surface area of the CaCO_3 present in the system of H.A. and hydroxyapatite increased, the intensity of infra-red at 3400 cm^{-1} also, increased. There were no serious variations between the absorption at 3400 cm^{-1} of H.A. treated with either hydroxyapatite or phytic acid. ----- As the C/H ratios of H.A. increased, the absorption intensity at $2920\text{--}2860\text{ cm}^{-1}$ also, increased either in presence or absence of KH_2P_4 . The absorption of H.A. at $1700\text{--}1725\text{ cm}^{-1}$ in the presence of KH_2P_4 greatly depends on their oxygen content and their C/O ratios. Application of humic acids with phytic acid, mostly increased their absorption at $1700\text{--}1725\text{ cm}^{-1}$, compared with those treated with hydroxyapatite. This is probably attributed to the lower adsorption of phytic acid on both H.A. and CaCO_3 than hydroxyapatite due to the greater molecule of the former compared with the later. The absorption of H.A. mixed with hydroxyapatite increased by increasing the surface area of CaCO_3 fractions present in the same system, that may suggest that the amount of hydroxyapatite adsorbed on H.A. mixed with fine limestone would be smaller than those mixed with coarse limestone. The values of H.A. intensity at 1300 cm^{-1} agree with their total C/N ratios content. 147 The ultra violet spectra indicated that the higher carbon content humic acid was the greater aromatic condensation and the more humified humic acid.

b) The ability of acids on the P solubility under the equilibrated systems. Half normal sodium hydroxide dissolved P, mostly more than ten times those dissolved by both H_2O and 0.5N NaHCO_3 due to the greater pH of the former, compared with the later. Humic acid dissolved in 0.5N NaOH extracted mostly more than ten times and more than one hundred times those extracted by both 0.5N NaOH and H_2O or 0.5N NaHCO_3 , respectively. Calcium chelation by humic acids in calcareous soil and limestone fractions

stimulate P solubilization and decreases its precipitation as calcium phosphate. The solubilization of P by different solutes from systems containing phytic acid and CaCO_3 greatly exceeded that solubilized from hydroxyapatite. These results are due to the higher solubility of phytic acid in the different solutes, compared with the very low solubility of hydroxyapatite. Phosphorus solubilization from systems containing the finest limestone yielded the lowest P values as compared with all the other systems. Humic acid in the gel form has a greater capability to solubilize P, compared with the dried form of humic acid.

C) Phosphorus adsorption isotherms: Data of P adsorption by different CaCO_3 sources, showed complete fitness to Langmuir adsorption isotherm in case of calcareous soil and oleitic limestone fractions. The previous equation was of fairly low efficiency in the case of the chemical compound, CaCO_3 (c.c.), that may be due to dominance of other mechanisms responsible for P sorption rather than to the one layer adsorption mechanism. According to Langmuir isotherm, there was no significant fitness for assessing P sorption in the systems containing humic acid, meanwhile this reliability was highly significant in case of either Van-Huay or Freundlich equation, that was the most reliable isotherm for such systems. The failure of Langmuir isotherm to describe the relation of P sorption in presence of humic acid may indicate the dominance of other reactions requiring higher bonding energy such as chemical reactions involving replacement of enolic or phenolic O-H groups. A close positive relationship between the maximum P adsorption (b) of Langmuir isotherm adsorbed on active surface and clay content, whereas a negative relationship with the affinity constant (K) was also, obtained. It seems that Van-Huay equation is more efficient for describing P sorption in such systems. Finally, it may be concluded that: humic acids are proved to be effective materials inducing P solubility in systems involving CaCO_3 which may suggest a controlling effect on P solubility due to these acids in such systems. The tested H.As can be arranged according to their solubilizing effect on P in the following order: Peanut H.A > farmyard manure H.A > Barley straw H.A. As the surface area of limestone fractions increased, the P solubility of the system decreased and parallelly increased the absorption of I.R at the wave length, characterizing the OH stretch which represent the main seat of P sorption. This phenomenon could be explained a basis of increasing the activity or potentials of Ca ions and hence the H_2PO_4 potentials decreased and/or precipitation reaction of $\text{Ca}_3(\text{PO}_4)_2$ that may take place at relatively higher P concentrations.