

Thesis Summaries

Organic Matter and Micronutrients in Some Soils of Peninsular Malaysia: Interactions and Influence on Plant Growth

The main objectives of the study were to characterise the nutrient status, especially the micronutrient status of some soils in Malaysia and to investigate the organic matter fractions of these soils. Having characterised and investigated the organic matter fractions of the soils, complexation or binding of the organic matter fractions with some micronutrients was also studied. This was followed by characterisation of the organo-metallic complexes. The effects of micronutrient application, presence of humic and fulvic acids and the interactions of the nutrients on plant growth and nutrient uptake were also studied.

Soils derived from igneous rocks of varying composition were analysed for the different forms of nutrients present. These soils are generally characterised by high clay and high total and free iron contents. Correlation studies on the various forms of nutrients with some soil variables such as particle size, percentage carbon and percentage free iron showed that total nutrient content was significantly correlated to silt, coarse sand and free iron content. Positive correlations were also observed to exist between silt/clay ratio (an index of weathering) and total iron, copper and manganese and between silt/clay ratio and extractable copper and manganese.

Extraction, fractionation and purification of humic substances from four of the soils studied were undertaken. Malaysian soils generally tend to have a greater amount of fulvic acid than humic acid. Physical and chemical tests showed that the clay minerals were linked quite strongly to the humic acid. Elemental and functional group analyses performed on the acids furnished some information on their structure and composition. Carbon and nitrogen contents of the humic acid were higher than those of fulvic acid while the oxygen and hydrogen contents were lower in the humic acid. Fulvic acid had higher total acidity and phenolic content than humic acid.

Chemical and physical tests showed some of the properties of the acids to be different from those reported in the literature. The equivalent weights of humic and fulvic acids, at seven days equilibration period, as estimated by the discontinuous titration method, were 153.00 g and 111.76 g respectively.

Complexation capacities of the purified fulvic and humic acids were determined by the ion-exchange equilibrium method of Crosser and Allen (1977). Three metal ions were used to determine the complexation capacities of the acids by this method. They are copper, zinc and manganese. The average values of the complexation capacities of humic and fulvic acids as estimated by the ion-exchange equilibrium method are $9.00 \times 10^{-4} M$ and $5.08 \times 10^{-4} M$ per gramme of humic acid and fulvic acid respectively.

Stability constants of the metal humates and metal fulvates were calculated. At pH 5 (the pH at which the reaction took place), the order of stability of the complexes formed is $Zn > Cu > Mn$ for the metal humates, and $Cu > Zn > Mn$ for the metal fulvates. It was concluded that the ion-exchange equilibrium method is fairly suitable for determining the complexation capacities of uncharacterised ligands forming soluble complexes, but not of ligands forming both soluble and insoluble complexes, for example humic acid with Cu^{2+} ions.

Binding abilities of the acids were also determined by a dialysis technique. The binding ability of the acid is a measure of the potential capacity of the negatively-charged macromolecules to bind or adsorb positively charged ions or molecules onto its active surface. The maximum binding ability of humic acid follows the order $Cu > Zn > Mn$, while for fulvic acid the order is $Cu > Mn \approx Zn$. The stability constants of the complexes formed and the moles of metal ions bound to one mole of the complexant were also calculated. From the results obtained, it was observed that mononuclear complexes of the 1:1 type were formed when the acids reacted with the metal ions at pH 5.

Following this, Cu, Zn, Mn and Fe humates and fulvates were prepared, purified and characterised by some physical and chemical tests. Chemical analysis showed that Zn was bound most to the humic acid. Cu, Mn and Fe were bound in roughly the same amounts. For fulvic acid Cu was bound most compared to Zn, Mn and Fe. Mechanisms other than complexation were believed to be responsible for the variations in the amounts of metal ions bound to the two acids.

Differences between the infra-red spectra of the complexes and those of the

starting materials were seen. Evidence from the infra-red spectra showed that in both acids, the metal ions were bound to both COO^- and OH^- functional groups.

Differential thermal analysis provided data on the main decomposition peaks of humic and fulvic acids and their complexes. It was observed that the main decomposition peak of humic acid was shifted to a higher temperature while the main decomposition peak of fulvic acid was shifted to a lower temperature on interaction of the acids with metal ions. The main decomposition peaks of the metal humates and fulvates were observed to lie in the same vicinity, that is in the range of $300^\circ C$ to $349^\circ C$.

The role of humic substances in regulating plant nutrients and their effects on plant growth were also investigated. Addition of either humic or fulvic acid was observed to result in improved plant growth, enhanced root development and subsequently higher nutrient uptake. When the micronutrients Cu, Zn, Mn and Fe were added in combination, the plants did not show different responses towards the addition of humic acid and fulvic acid. However, when the micronutrients were applied singly, there were different responses by the plants between the addition of humic acid and fulvic acid. The addition of fulvic acid generally resulted in higher dry matter yields and nutrient uptake than the addition of humic acid. This was believed to be due to the less complex nature and smaller size of fulvic acid compared to humic acid. Being smaller and less complex, absorption of fulvic acid by plants would be easier.

From observations of pot experiments and statistical analysis of the data, significant interactions exist between the different NPKMg combinations and micronutrients. Thus, it is stressed here that,

such interactions should be taken into account when applying micronutrients to plants.

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Short Fibre Woodcellulose as a Filler for Natural Rubber

The effect of unregenerated short cellulose fibres from woodpulp on the properties of rubber vulcanisates and the type of woodpulp able to produce short fibre-rubber composites of good physical properties at a reduced cost were investigated. A screening procedure was carried out to identify one particular type of woodcellulose short fibre for detailed investigation. Mechanical woodpulp containing short cellulose fibres were selected based on their dispersibility properties in rubber, low cost, and universality of application.

Among various types of bonding agents studied, a resorcinol-hexamethylenetetramine (RH) system was found to be most effective to bond woodcellulose fibre (mechanical type) to natural rubber matrix. This was judged by certain properties namely, restricted equilibrium swelling, yield stress and tear strength.

Restricted equilibrium swelling in particular was established to be a very useful technique by which the degree of adhesion can be predicted. In this technique, the short fibre-rubber composites were swollen in toluene for one week, after which, the volume restriction value, V_r , was calculated using the formula:

$$V_r = \frac{V_I - V_F}{V_I}$$

where V_I and V_F are the volume fractions of rubber in dry and swollen samples respectively. Based on V_r value, it has been observed that, with the exception of silane, all bonding systems studied improved woodcellulose fibre-natural rubber adhesion.

Optimisation work to determine the optimum level of resorcinol-hexamethylenetetramine combination was also carried out based on a statistical factorial experimental design, in particular the 'central composite design'. Contour graphs of different properties of compounds for various levels of bonding agent combination were obtained by means of computer programmes. From these contour graphs it was established that the combination of three parts of hexamethylenetetramine (HMT) and four parts of resorcinol gave the best overall properties.

The RH bonding system studied, besides functioning as a bonding agent, was also found to crosslink rubber chains through the formation of resin during high temperature vulcanisation process; a mechanism of this chemical reaction was postulated.

Mechanical properties of composites containing optimum level of resorcinol-HMT combination measured in the direction of fibre orientation have indicated their dependence on fibre concentration. Young's modulus in particular increased exponentially with increasing fibre concentration. Experimental and theoretical curves of Young's modulus *versus* volume concentration of fibres showed good correlation up to fibre volume concentration of 30%; beyond which increasing divergence occurred.

Besides physical and mechanical properties, the cost factor of woodcellulose fibre-rubber composite was also considered. Cost advantage was clearly evident as a result of incorporation of

woodcellulose fibre in natural rubber compound.

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Coagulant Dipping of Natural Rubber Latex

A detailed study has been made of the coagulant dipping of natural rubber latex using calcium chloride as the coagulant. The primary object of the investigation was to deepen understanding of the kinetics and mechanisms of deposition. Results are given for the effect of variables such as solids content, latex viscosity, added fatty-acid soap, amount of calcium on the former, added non-ionic surfactants and latex pH upon the thickness-time relationship in the coagulant dipping process. All, except the initial amount of calcium on the former, were found to have little effect upon the wet thickness-time relationship. The relationship between the wet deposit

thickness and the square root of the dwell time was found to be linear.

An investigation has also been made into the fate of the calcium ions during the dipping process. It was found that the deposition of rubber on the former involves reaction between the cations of the coagulant and the adsorbed anions which stabilise the latex. Fatty-acid anions and other unknown anions were found to react with the calcium ions.

The process was found to be diffusion-controlled. The diffusion coefficient of calcium ions in the latex gel was calculated to be approximately $1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. However, the assumptions made in deriving this value are such that it should be viewed with suspicion until confirmed by further experimentation and analysis.

The mechanisms of deposition have been postulated to involve dehydration of the latex particles, neutralisation of the fatty-acid anions adsorbed on the latex particles and there is some evidence for compression of the double layers.

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