Availability of Humate Potassium

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Chemically, one of the outstanding properties of humic acid is that of holding bases such as potassium in an exchangeable or readily available form. This form of potassium will be referred to hereinafter as humate potassium.

Although humus or humic acid accounts for 30 to 60% of the base exchange capacity of many soils, little information exists concerning either the conditions affecting the availability of humate potassium, or the relative availability of humate potassium compared to that held by clay minerals in exchangeable form. Truog and Jones (10) indicated that the introduction of organic matter, which supplies organic base exchange material, would lessen the fixation of potassium into the nonexchangeable form by clay minerals.

Joffe and Kolodny (4, 5) reported that organic matter did not fix potassium in a nonexchangeable form. Other investigators (3, 9, 12) have pointed out that organic matter exerts a repressive effect on the power of soils to fix potassium in nonexchangeable form.

Loehwing (6) reported that grain crops grown on acid muck are often injured by the addition of calcium carbonate which may engender potassium hunger. This was not verified by the work of Enfield and Conner (2).

The purpose of this study was to investigate the influence of pH and degree of calcium saturation of humic acid on the availability of humate potassium, and to compare the relative availability of humate potassium to potassium held in exchangeable form by clay minerals.

EXTRACTION OF HUMIC ACID
AND ITS PURIFICATION

Obviously, in order to study the availability of humate potassium, it is desirable to use humus which is as free of extraneous material as is possible. A review of the literature pertaining to humic acid as ordinarily separated from soils and purified revealed that on ignition this product generally leaves a mineral residue of 2 to 10%. Whether or not this residue is an essential constituent of humus is open to question. The first step in this study was to prepare humic acid as pure and free of mineral matter as possible.

SOLUTIONS USED

1. Sodium chloride, 10%, pH 3.—Dissolve 100 grams of sodium chloride and 0.4 ml of concentrated HCl in 1 liter of water.
2. Sodium chloride, 10%, pH 9.—Dissolve 100 grams of sodium chloride, 2 grams of NaCO₃, and 2 grams of NaHCO₃ in 1 liter of water.
3. NaCO₃-NaHCO₃ extracting solution, pH 9.—Dissolve 0.25 gram of NaCO₃ and 2 grams of NaHCO₃ in 1 liter of water.
4. Hydrofluoric acid, 0.12N, pH 2.—Dilute 5 ml of 48% HF to 1 liter with water. Adjust to pH 2 with 48% HF, using thymol blue indicator.

DETAILS OF PROCEDURE ADOPTED

After a number of preliminary tests, the following procedure for extraction of humus was adopted:

1. A 50-gram sample of mineral soil or a 20-gram sample of peat is placed in a 500-ml Erlenmeyer flask and added 200 ml of the sodium chloride solution of pH 9. The suspension is shaken for 30 minutes on a mechanical shaker or allowed to stand overnight. It is then filtered by means of a Whatman No. 2 filter paper placed on a 1,000-ml suction flask. The leachate continued with an additional 200 ml of the same solution followed with 500 ml of the sodium chloride solution.

The filtrate is discarded. The soil is now ready for the extraction of sodium humate by leaching with 500 ml of NaHCO₃-NaCO₃ solution, using 100 ml aliquots. The first 100 ml have been drawn through the humus; a sufficient dispersion to allow its extraction, but it is not certain that the extracting solution be no more alkaline than pH 9 or the clay will disperse and clog the filter. Generally, eight 50-gram samples of soil are extracted sequentially in order to finally obtain a workable amount of the humic acid.

2. The Na-humate solution is run through a Sharpies centrifuge at such a rate (32,000 rpm) that the colloidal solution in the bowl long enough to sediment the particles 0.014 in diameter.

3. The centrifuged humate solution is adjusted with dilute HCl, causing coagulation of the humate, then placed in 100-ml centrifuge tubes which are clouded for 15 minutes at 2,000 rpm. The supernatant liquid is poured off. At no time is the humic acid allowed to become dry.

4. In order to dissolve and remove the very fine material which is invariably present as a contaminant, the humate is treated with HF of pH 3. To do this the humic acid is transferred to centrifuge tubes which have been coated with a film of paraffin. Ten ml of 0.12N hydrofluoric acid and sufficient water are added to bring the volume of each tube to 35 ml. After thorough mixing, the suspension is clotted for 30 minutes at 2,000 rpm. The supernatant liquid is poured off, after which the suspension is again brought to 35 ml and a pH of 3 by adding the necessary water and 1 ml of 0.12N hydrofluoric acid. After mixing and centrifuging as before, the supernatant liquid is poured off. This is repeated until the supernatant liquid becomes clear and three treatments suffice. The humic acid is finally transferred to ordinary centrifuge tubes and the suspension brought to 50 ml with water and adjusted to pH 3 with dilute HCl.

5. In order to remove the difficulty soluble iron which always persists as a contaminant, the centrifuged humic acid suspension is placed in a water bath and slowly heated to 60 to 60° C; a magnesium ribbon is inserted into each tube and left there for about 10 minutes, causing evolution of nascent hydrogen which reduces the iron and makes it soluble. The tubes are centrifuged for 30 minutes at 2,000 rpm. The supernatant liquid is poured off, and the solution is again suspended in a NaCO₃-NaHCO₃ solution of pH 9. The colloid is again suspended in 50 ml of water, adjusted with NaHCO₃ and the above reducing procedure is repeated until the supernatant liquid gives no test for iron after three treatments suffice.

6. The humic acid is next suspended in 50 ml of a NaHCO₃ solution and the suspension is centrifuged for 30 minutes at 2,000 rpm. The supernatant liquid is poured off and the residue is suspended in 10 ml of 0.12N hydrofluoric acid and 20 ml of water. The suspension is placed in a water bath and heated to 60° C; a magnesium ribbon is inserted into each tube and left there for about 10 minutes, causing evolution of nascent hydrogen which reduces the iron and makes it soluble. The tubes are centrifuged for 30 minutes at 2,000 rpm. The supernatant liquid is poured off, and the solution is again suspended in 50 ml of water, adjusted with NaHCO₃ and the above reducing procedure is repeated until the supernatant liquid gives no test for iron after three treatments suffice. The resulting humic acid is finally centrifuged at 2,000 rpm for 30 minutes, the supernatant liquid is poured off and the residue is washed with 10 ml of water, adjusted with NaHCO₃ and the above reducing procedure is repeated. The resulting solution is then ready for analysis.

This procedure, although not without its limitations, has given good results. It is important to note that the humic acid is not completely dissolved in the NaCO₃-NaHCO₃ solution and that the solution is cloudy. This is due to the presence of a colloidal substance which is still present in the humate.