

EFFECT OF HUMIC SUBSTANCES ON SOLUBILITY OF INSOLUBLE  
MINERAL PHOSPHATE COMPOUNDS

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تأثير المواد الدبالية على ذوبان مركبات الفوسفور المعدنية الغير نائية

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ملخص البحث

تم دراسة تأثير زمن التفاعل وال pH ومستويات مختلفة من حامض الفلبيك والهيوميك على ذوبان مركبات الفوسفور المعدنية الغير نائية ( خبت المعانين وصخر الفوسفات ) .

وصفة عامة وجد أن تأثير حامض الفلبيك على ذوبان مركبات الفوسفور الغير نائية أعلى من حامض الهيوميك . كما وجد أن الفوسفور الذائب من خبث المعانين كان أعلى منه في حالة صخر الفوسفات ، واتضح من النتائج أن ذوبان الفوسفور من مركباته المعدنية يزداد بزيادة زمن الرج حتى ١٦ ساعة . ولكن وجد أن معدل التغير في الفوسفور الذائب يقل مع زيادة زمن الرج .

وكذلك أظهرت النتائج أن الفوسفور الذائب يقل بزيادة ال pH من ٤ حتى ٦ ثم عند pH ٨ ، ولكنه يزداد عند كلا من pH ٧ و ٩ .

وأيضاً أوضحت النتائج زيادة ذوبان الفوسفور من مركباته الغير نائية بزيادة تركيز الأحماض المستخدمة ولكن وجد أن معدل التغير في ذوبان الفوسفور يقل بزيادة كمية الأحماض .

## ABSTRACT

The effect of shaking time, pH, and varying levels of fulvic and humic acids on the solubility of insoluble mineral phosphate compounds, namely, basic slag and rock phosphate was studied in a soil-free contact. In general, efficiency of fulvic acid on the solubility of phosphate compounds was higher than that of humic acid. Release of soluble P from the basic slag was greater than from rock phosphate. Solubility of P was increased with increasing each of the amount of acids used and shaking time up to 16 hrs. Availability of insoluble phosphate was decreased at pH 4.0 to 6.0 then at 8.0 but increased at each of pH 7.0 and 9.0.

## INTRODUCTION

Solubility of phosphate in soil is influenced by kind of chemical compounds present, but it is generally low under all conditions. Factors favouring phosphate solubility are the following: 1) a good supply of readily decomposable organic matter, 2) a pH between 6.5 and 7.5, 3) a high level of phosphorus, 4) a substantial level of moisture, and 5) a high silica: sesquioxide ratio.

Mechanisms of interaction of organic matter with mineral fraction of soils may vary quite widely in nature. This has been amply demonstrated in many studies (Leaver and Russell, 1957; Datta and Shrivastava, 1963). Weir and Soper (1963), Levesque and Schnitzer (1967), and Fokin and Sinha (1969) reported that the solvent action of humic substances was due to the formation of fulvic acid-metal phosphate. Barbier *et al.* (1951) and Fokin and Chistova (1964) proposed that the derived benefits of adding organic matter to the soil were due to anion replacement or competition between humate and phosphate ions for sites on the adsorption surface. Sinha (1972) found that fulvic acid and intermediate products of organic matter decomposition play a significant role in the mobilization of difficultly soluble phosphate.

The aim of this research was to study the effect of fulvic and humic acid concentrations, shaking time, and pH of medium on the solubility of insoluble inorganic phosphate compounds in a direct soilless interaction.

## MATERIALS AND METHODS

### A. Separation of fulvic and humic acids:

A surface soil sample (0-30 cm) of an alluvial soil was taken from the Experimental Farm, Fac. of Agric., Shebin El-Kom. The sample was air-dried, ground, and passed through a 2-mm sieve. Some physical and chemical properties of the soil are presented in Table (1). The isolation and purification method of humic acid described by Posner (1966) was followed. The sample was extracted with 0.5 N NaOH (Soil : extractant ratio was 1:5). The mixture was shaken mechanically for 3 hrs, allowed to stand overnight; and the supernatant was collected by centrifugation for 20 min. at 6000 rpm. The solution obtained was acidified with 1.0 N HCl to pH 1.5 to precipitate humic acid. The supernatant was the fulvic acid fraction, and the precipitate was the humic acid fraction of soil humus. Humic acid was separated from solution by centrifugation, washed with 0.5% HCl:HF (1:1) solution, dialyzed and then air-dried. The solution of fulvic acid was concentrated by evaporation in a hot-air oven, then purified by passing twice over large columns of Amberlite IR-120 exchange resin in H-form and Amberlite IR-45 exchange resin in OH-form (Schritzer and Gupta, 1964). The elementary composition of fulvic and humic acids is shown in Table (2).

### B. Treatments:

Two compounds were chosen as insoluble inorganic phosphate sources, namely, basic slag (by-product of iron industry) and rock phosphate (carbonate apatite). The compounds were milled and passed

Table (1): Analytical data of the investigated soil.

## a) Physical properties:

Organic matter %	CaCO <sub>3</sub> %	Particle size distribution %			Textural grade
		Sand	Silt	Clay	
2.15	2.80	27.02	27.02	45.96	Clay

## b) Chemical properties:

pH (1:2.5)	E.C. mmho/cm	C.E.C. meq/100g	Soluble ions (meq/100 g)							
			Cations				Anions			
			Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>--</sup>	SO <sub>4</sub> <sup>--</sup>
7.90	0.44	28.60	0.80	0.45	1.12	0.33	0.80	0.95	-	0.95

Table (2): Elementary composition of humic and fulvic acids.

Humic substance	Percent on the oven-dry ash-free basis				Ash
	C	H	N	O*	
Humic acid	54.7	4.5	3.8	37.5	0.18
Fulvic acid	46.1	5.8	1.2	46.9	0.95

\* By difference.

Table (3): Chemical composition of insoluble mineral phosphatic compounds used.

Insoluble phosphate	P <sub>2</sub> O <sub>5</sub> %	CaO %	MgO %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %
Basic slag	15.21	42.52	1.82	0.11	8.86
Rock phosphate	31.51	40.10	1.54	6.52	2.51

through 1-mm sieve. Some chemical properties of these compounds are presented in Table (3).

Effect of shaking time, at room temperature ( $25\pm 2^\circ\text{C}$ ), on the reaction between 25 mg fulvic or humic acid with 0.01 mg P of basic slag or rock phosphate was studied at varying periods, i.e. 1, 2, 4, 8, 16, and 24 hrs of contact at pH 7.0, then centrifuged for 20 min. at 6000 rpm. The supernatant was taken to dryness on a steam bath and digested with a mixture of 3:1 conc.  $\text{H}_2\text{SO}_4:\text{HClO}_4$ . The solution was made up to 25-ml volume with distilled water and the phosphorus was determined colourimetrically using stannous chloride method (Jackson, 1958).

Effect of pH on the reaction between fulvic or humic acid and either insoluble phosphate compound was studied by adding 25 mg of fulvic or humic acid to 0.01 mg P of basic slag or rock phosphate. pH of the mixture was adjusted to 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0. The volume was made up to 25 ml with distilled water and shaken for 16 hrs at room temperature ( $25\pm 2^\circ\text{C}$ ) and centrifugated for 20 min. at 6000 rpm. The supernatant was analyzed as mentioned above.

Controls using distilled water rather than humic substances were simultaneously performed for each of the above two experiments.

Aliquotes containing 0.5, 10, 15, 20, 25, and 50 mg of fulvic or humic acid solution were transferred into glass tubes, then the volume was made up to 15 ml with distilled water. Basic slag or rock phosphate was added to each tube at a rate of 0.01 mg P.  $\text{pH}$  of the medium was adjusted to pH 7.0 with 0.01 N HCl or 0.01 N NaOH as required. The final volume was made up to 25 ml with distilled water. The suspensions were shaken for 16 hrs at room temperature ( $25\pm 2^\circ\text{C}$ ) and centrifuged for 20 min. at 6000 rpm. The supernatant was analyzed as mentioned above.

## RESULTS AND DISCUSSION

Effect of time of shaking on the percentage solubility of P from its insoluble mineral compounds (basic slag and rock phosphate) by fulvic and humic acids is shown in Table (4). Data indicated that values of soluble P produced from its tested compounds revealed slight increase with increasing the shaking time up to 16 hours, thereafter, no further worthy increments were obtained. Therefore, the 16-hour shaking time was selected for consequent studies. The percentage recovery, showed sharp decreases by advancing the time of contact. This means that the reaction between the humic substances and the phosphate compounds occurs vigorously at the initiation of contact then proceeds at a low extent of increase. Data also (Table 4) implied that fulvic and humic acids increased the soluble P, released from both sources under consideration, when compared with the distilled water. The increase was 100 and 71 times as much as the distilled water for fulvic acid, while it was 80 and 55 times for humic acid from basic slag and rock phosphate respectively. The effect of fulvic acid on the solubility of P from its insoluble compounds was higher than that from humic acid at all times studied. These findings agree with those of Sinha (1972) who found that, fulvic acid predominates over other forms of humic substances in soil solution. The present results also indicated that, the effect of fulvic acid and humic acids on the release of P from the basic slag was higher than that from the rock phosphate at all intervals examined. This might be due to the high content of  $Al_2O_3$  in the rock phosphate (Table 3). In such connection, Sinha (1972) found that the influence of straw decomposition on the release of phosphate was evident only with  $Ca_3(PO_4)_2$  and  $FePO_4$ , whereas the solubility of  $AlPO_4$  was practically not affected.

Effect of pH of the medium on the percentage solubility of P from its insoluble compounds by the action of fulvic and humic acids

**Table (4):** Effect of time of shaking the fulvic and humic acids with insoluble phosphate compounds on the percentage solubility of phosphorus at pH 7.0.

Insoluble phosphate compounds	Shaking time in hrs					
	1.0	2.0	4.0	8.0	16.0	24.0
Percentage recovery of soluble phosphorus						
Distilled water						
Basic slag	0.003	0.003	0.004	0.004	0.004	0.004
Rock phosphate	0.002	0.002	0.002	0.003	0.003	0.003
Fulvic acid (25 mg)						
Basic slag	0.333	0.344	0.365	0.396	0.426	0.426
Rock phosphate	0.114	0.130	0.144	0.153	0.164	0.164
Humic acid (25 mg)						
Basic slag	0.274	0.277	0.280	0.306	0.317	0.318
Rock phosphate	0.088	0.110	0.124	0.132	0.136	0.136

**Table (5):** Effect of pH on the percentage recovery of soluble phosphorus shaken for 16 hrs with fulvic and humic acids.

Insoluble phosphate compounds	pH					
	4.0	5.0	6.0	7.0	8.0	9.0
Percentage recovery of soluble phosphorus						
Distilled water						
Basic slag	0.003	0.002	0.002	0.003	0.002	0.003
Rock phosphate	0.005	0.003	0.004	0.004	0.004	0.004
Fulvic acid (25 mg)						
Basic slag	0.573	0.512	0.470	0.486	0.405	0.486
Rock phosphate	0.225	0.197	0.153	0.164	0.150	0.186
Humic acid (25 mg)						
Basic slag	0.417	0.378	0.307	0.319	0.285	0.431
Rock phosphate	0.193	0.140	0.116	0.136	0.123	0.156

is shown in Table (5). Both acids surpassed the distilled water in enhancing the solubility of P from both sources at all pH values tested. Influence of fulvic acid on such concern was higher than that of humic acid, and both acids were more effective on basic slag than on rock phosphate at all of the experimental pH values. Results also declared that, amount of soluble P was decreased at the acidic pH, i.e. 4.0 to 6.0, and increased at the neutral pH 7.0. However, at pH 8.0 a diminution in soluble P was observed, but at pH 9.0 value soluble P was again raised. Explanation of this behaviour could be as follows: a) At low pH (below 6.5) large amounts of Fe and Al in solution readily combine with P released by humic substances to form compounds which are relatively less soluble, or react with humic substances to form insoluble compounds which in turn reduce the effect of humic substances in releasing P, b) At pH 6.5, the amounts of Fe and Al in solution are considerably lower and hence more available P is present in the medium, or humic substances are more effective on the release of P in this case, c) Above pH 7.5, more Ca and Mg ions are present in the solution which are able to combine with the phosphorus released to form less soluble compounds, or react with humic substances to form insoluble compounds which reduce the effect of humic substances in releasing P, and d) At pH 8.5 to 10.0, the added  $\text{Na}^+$  ions are the dominating cations and combine with phosphate anions to form sodium phosphate which is highly soluble, or react with humic substances to form more soluble compounds. Ong and Bisque (1968) noted that, at pH 7.0 trivalent ions are more effective on coagulation of humus than divalent ions, and divalents are in turn more effective than monovalent ones.

Data drawn in Fig. (1) illustrate the influence of varying concentration of fulvic and humic acids on the mobilization of P from its insoluble inorganic compounds. Soluble P was increased with increasing the amount of acids added. Similar results were



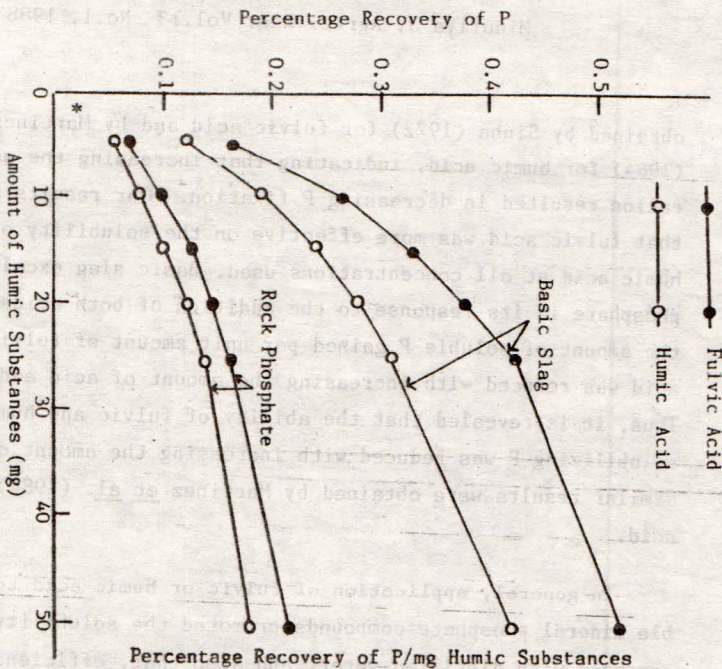


Fig. (1): Percentage release of soluble P from its insoluble compounds shaken with Fulvic and humic acids (25 mg each) for 16 hrs at pH 7.0.

\* Values of distilled water were too low to be presented in the figure at the tracing scale used.

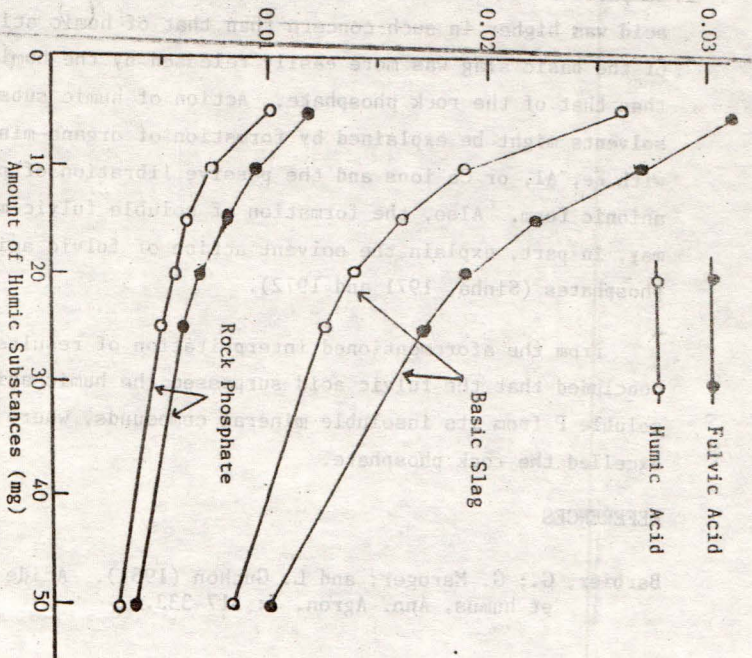


Fig. (2): Change in the rate of soluble P per unit amount of humic substances after shaking for 16 hrs at pH 7.0.

obtained by Sinha (1972) for fulvic acid and by Martinez et al. (1984) for humic acid, indicating that increasing the acid concentration resulted in decreasing P fixation. Our results also denote that fulvic acid was more effective on the solubility of P than humic acid at all concentrations used. Basic slag excelled the rock phosphate in its response to the addition of both acids. Rate of the amount of soluble P gained per unit amount of fulvic or humic acid was reduced with increasing the amount of acid added (Fig. 2). Thus, it is revealed that the ability of fulvic and humic acids in solubilizing P was reduced with increasing the amount of acid added. Similar results were obtained by Martinez et al. (1984) for humic acid.

In general, application of fulvic or humic acid to the insoluble mineral phosphate compounds promoted the solubility of P when compared with distilled water, and also that, efficiency of fulvic acid was higher in such concern than that of humic acid. Phosphorus of the basic slag was more easily released by the humic substances than that of the rock phosphate. Action of humic substances as solvents might be explained by formation of organo-mineral complexes with Fe, Al, or Ca ions and the passive liberation of phosphate in anionic form. Also, the formation of soluble fulvic-metal phosphate may, in part, explain the solvent action of fulvic acid on inorganic phosphates (Sinha, 1971 and 1972).

From the aforementioned interpretation of results, it may be concluded that the fulvic acid surpassed the humic acid in releasing soluble P from its insoluble mineral compounds, where basic slag excelled the rock phosphate.

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