Solubilization of rock phosphate by humic and fulvic acids extracted from atraw compost

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INTRODUCTION. – The direct utilization of low-grade rock phosphate as phosphatic fertilizer is possible through composting it with ligno-cellulosic wastes (SINGH & AMBERGER, 1991; KUBÁT et al., 1985). The solubilization of P from rock phosphate during composting largely depends on the kind of organic waste and the rate of organic matter decomposition.

LEVESQUE & SCHNITZER (1967) and SINHA (1972) reported that humic substances resulting from organic matter decomposition played a significant role in mobilizing insoluble phosphates, whereas other workers indicated that organic acids and intermediate products of organic matter decomposition were mainly responsible for solubilization of inorganic phosphates (GAUR & PAREEK, 1974; ESTAUN, 1974). STEVENSON (1982) proposed that insoluble phosphate was solubilized through the combined action of organic acids, humic substances and carbonic acid from CO_2 produced during the decay of organic matter. Most of the investigations were conducted in systems of soil organic matter and hardly recognized any effect on mobilization of insoluble P from low-grade rock phosphate as a result of production of variable and small amounts of humic substances. However, in a compost system, large quantities of humic and fulvic acids are produced (Singh & Amberger, 1990), which may have a greater effect on P solubilization. The importance of a study of direct utilization of low-grade rock phosphate through composting led us to quantify the solubilizing capacity of humic and fulvic acids extracted from wheat straw compost.

EXPERIMENTAL. - Humic and fulvic acids, extracted with 0.1 N NaOH solution from wheat straw compost, were purified using the method of

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SCHNITZER (1988). Humic and fulvic acids contained 4.52 and 4.98% ash, 57.31 and 47.04% carbon, 8.9 and 11.52 m mole g^{-1} total acidity, and 3.4 and 7.90 m mole g^{-1} of carboxyl groups, respectively.

Both rock phosphates are from sedimentary rock and fall in the low grade category because of their low P_2O_5 and high $CaCO_3$ contents. MP has pH 7.85 (1:2 RP - water suspension) and contains 19.5% total P_2O_5, 1.38% formic acid-soluble P_2O_5, 20.3% $CaCO_3$ and 1.61% organic carbon; HP has pH 8.3 (RP-water suspension) and contains 30.48% total P_2O_5, 20.57% formic acid-soluble P_2O_5, 16.17% $CaCO_3$ and 0.27% organic carbon.

The amount of rock phosphate can be an important factor in P-solubilization with HA and FA because both rock phosphates contain very high content of free $CaCO_3$. Therefore, different ratios of RP to HA or FA were tried to get the maximum solubilization. The solubilization was determined by placing 20 ml of 0.5 mg ml^{-1} HA and FA concentration separately in a number of glass stoppered tubes. Variable amount of MP and HP ranging from 10 to 500 mg were added separately in duplicate and then tubes were shaken for 24 h at 30 ± 1°C. After measuring equilibrium pH, the mixture was centrifuged and HA and FA were eliminated from supernatant by treating with $HClO_4$ at 160°C. The P was determined by the method of John (1970) and other cations such as Ca, Mg, Na, K, Zn and Fe by an Atomic Absorption Spectrophotometer.

To learn about the nature of interaction, another experiment was conducted in similar way by keeping the ratio of 4:1 for RP to HA and 6:1 for RP to FA. Duplicate tubes were taken for P determination at different time intervals ranging from 15 minutes to 24 h.

RESULT AND DISCUSSION. — Both MP and HP did not have P solubility in aqueous solution. The data on equilibrium pH and P solubility at different ratios of RP to HA or FA are presented in Table 1. The result shows that the release of P increased with increasing amount of rock phosphate up to 4:1 RP to HA ratio when pH of the equilibrium reached 6.2. On further increasing the ratio of RP to HA, the release of P decreased gradually along with increasing the equilibrium pH and P solubilization became zero at pH 7.35 in case of HP. The slow release of P at initial RP:HA ratios in spite of low equilibrium pH, was mainly due to high $CaCO_3$ content of RP. HA first neutralizes the free $CaCO_3$ and then solubilizes the loosely bound P or moderately soluble dicalcium phosphate as shown formic acid soluble-P fraction in both rock phosphates. At wide RP to HA ratios, the amount of free $CaCO_3$ increased so much that it consumed whole of HA instead of solubilising P-minerals. The highest P solubilization ie. 9.36 and 11.19

μg^{-1} HA, respectively was observed from MP and HP at 4:1 ratio. The higher release of P from HP was mainly due to presence of higher amount of formic acid soluble dicalcium phosphates.

TABLE 1. – *Influence of wheat straw HA and FA on the solubilization of low grade rock phosphates (RP).*

RP:HA/FA ratio	RP added (mg)	Mussoorie phos			Hyper phos		
		Equili-brium pH	P in solution ($\mu g\ ml^{-1}$)	Solubi-lized ($\mu g\ mg^{-1}$ HA/FA)	Equili-brium pH	P in solution ($\mu g\ ml^{-1}$)	Solubi-lized $\mu g\ mg^{-1}$ HA/FA)
Humic acids (HA)							
0:1	0	4.43	0	0	4.43	0	0
1:1	0	4.81	2.62	4.24	4.66	2.94	5.89
2:1	20	5.52	3.85	7.70	4.89	4.52	9.04
4:1	40	6.20	4.68	9.36	6.18	5.59	11.19
6:1	60	6.46	4.06	8.13	6.61	3.69	7.38
10:1	100	6.67	2.93	5.96	6.92	2.37	4.74
20:1	200	6.97	1.43	2.96	7.16	0.50	1.00
50:1	S00	7.18	0.64	1.28	7.35	0	0
Fulvic acids (FA)							
0:1	0	2.74	0	0	2.74	0	0
1:1	0	3.85	4.91	9.82	3.66	5.75	10.50
2:1	20	4.57	7.00	14.00	4.68	8.23	16.47
4:1	40	5.43	8.43	16.86	5.20	10.07	20.14
6:1	60	6.22	9.08	18.16	6.18	10.71	21.43
10:1	100	6.89	6.56	12.32	6.95	6.12	12.24
20:1	200	6.07	1.50	3.00	6.51	1.06	2.12
50:1	500	7.17	0.62	1.24	7.35	0	0

HA or FA concentration, 0.5 mg ml^{-1}. Total volume, 20 ml.

In case of FA the release of P reached highest ie. 18.16 and 21.43 $\mu g\ mg^{-1}$ FA respectively, from MP and HP at 6:1 RP to FA ratio. At this stage, FA had abaut 80% higher P solubilizing capacity than HA because of containing low initial pH due to possession of higher amount of COOH group. The release of P from HP also became zero when equilibrium pH touched to 7,35 at the highest level of (500 mg) of RP added. In case of HP the equilibrium pH increased rapidly at wide ratios than MP due to release of very high content of sodium (Table 2). The solvent action of HA/FA on insoluble phosphate may be explained on the

basis of Ca chelation with HAs and FAs or the formation of their water soluble compounds and passive liberation of P in ionic form.

Some cations also released during the dissolution of both rock phosphates (Table 2). The concentration of Ca, Zn, and Fe increased continuously up to 4:1 RP to HA and 6:1 RP to FA ratio and then decreased gradually on increasing the ratios. The decrease in the concentration of these cations and P in the same ratio indicated that solubilized P again precipitated when equilibrium pH increased more than 6.18 on widening the ratios. The release of Na, Mg and K increased continuously with increasing amount of RP and reached maximum at highest ratio of RP to HA or FA even P-solubilization became zero. This shows that these three elements are not substituted in P-bearing mineral apatite. The Ca, Na, and K contents were comparatively released in higher quantities from HP than from MP while Zn concentration was lower and Fe was found totally absent in the former. FA extracted all cations in higher quantities than HA.

TABLE 2. – *Influence of HA and FA on the release of cations ($\mu g\ ml^{-1}$) from low grade rock phosphates.*

RP: HA/FA ratio	Mussoorie phos						Hyper phos					
	Ca	Mg	Na	K	Zn	Fe	Ca	Mg	Na	K	Zn	Fe
Humic acids												
0:1	0	0	0	0	0	0	0	0	0	0	0	0
1:1	20	0.9	0.7	0.1	0.3	0.2	38	1.1	2	1	0.4	0
2:1	42	1.0	0.9	0.1	1.1	0.3	67	1.1	4	2	0.6	0
4:1	60	1.2	1.1	0.2	0.3	0.4	91	1.3	8	7	0.8	0
6:1	55	1.4	1.2	0.3	1.0	0.3	70	1.6	12	10	0.5	0
10:1	49	1.7	1.3	0.5	0.8	0.3	50	2.1	18	16	0.4	0
20:1	33	2.7	1.7	0.8	0.6	0.3	21	3.0	29	32	0.2	0
50:1	27	4.6	1.6	1.0	0.2	0.1	20	5.4	52	55	0.1	0
Fulvic acids												
0:1	0	0	0	0	0	0	0	0	0	0	0	0
1:1	22	0.7	5.0	1.5	1.3	0.8	38	1.1	30	2	2.1	0
2:1	53	2.1	5.0	1.7	2.9	1.5	69	1.6	35	5	2.5	0
4:1	75	4.2	5.0	2.0	4.0	1.9	91	2.0	40	10	2.6	0
6.1	84	5.3	5.0	2.3	4.3	2.1	110	3.2	45	15	2.7	0
10:1	60	6.4	5.0	2.5	2.7	0.4	73	5.2	50	20	1.6	0
20:1	52	6.7	5.0	2.9	1.6	0.2	58	6.4	60	25	1.1	0
50:1	52	6.5	5.0	3.0	0.1	0.1	47	7.1	100	45	0.1	0

HA and FA concentration, 0.5 mg ml^{-1}. Total volume, 20 ml.

The integration method was used to analyze the kinetic data (Table 3). We assumed a first-order reaction which can be expressed by the following integrated first-order rate equation.

$$\log C = \log C_o - \frac{K}{2.303} t$$

Where

C_o = amount of insoluble P in the volume of acid used per gram of rock phosphate at the start of the reaction, that is the same as the amount of insoluble P per gram of rock phosphate; C = amount of insoluble P in the volume of acid used per gram of rock phosphate at time t; K = rate of reaction, and t = time.

TABLE 3. – *Kinetic data of HA and FA - Rock phosphate interaction.*

Time (h)	Humic acids		Fulvic acids	
	MP	HP	MP	HP
		P in solution (μg ml^{-1})		
0	0	0	0	0
0.25	1.97	3.02	6.60	8.12
0.50	2.40	3.12	7.18	8.66
1.00	2.90	3.72	8.13	9.13
1.50	3.40	4.42	9.23	10.05
2.00	4.17	5.17	9.20	10.05
2.50	4.63	5.65	9.23	10.05
3.00	4.60	5.63	9.20	10.08
5.00	4.62	5.62	9.21	10.10
24.00	4.63	5.65	9.20	10.05

HA and FA concentratioan, 0.5 mg ml^{-1}. Total volume, 20 ml.

As per methods and material, 500 ml HA and 333 ml FA are required to dissolve maximum amount of P from one gram of RP, respectively at 4:1 RP to HA and 6:1 RP to FA ratio. The initial added insoluble P (C_o) was 85.184 mg per gram of MP and 133.082 mg per gram of HP. The amount of insoluble P (C) at each time interval was calculated by subtracting the value of solubilized P (mg P per S00 ml HA or 333 ml FA) from initial added P (mg P g^{-1} of RP) from both rock phosphates.

The reaction was completed with in 2.5 and 1.5 h respectively, in HA and FA, and thereafter constant values of solubilized P were

obtained up to 24 h, most probably due to neutralization of whole organic acids or remaining of more resistant P-bearing minerals (Table 3). Most of the P was solubilized in less than 15 minutes in all the cases. Therefore, the values of log C were plotted against t from 15 minutes to 2.5 h for HA and from 15 minutes to 1.5 h for FA (Fig. 1). All the four curves were found linear which confirmed the first-order reactions. The linear equations, correlation coefficients and rates of reaction for the linear curves are listed in Table 4. The intercept of the straight line on log C axis is lower than the logarithm of the initial concentration of C_o (for MP 1.9303, for HP 2.1241) in all the cases, indicating that for time shorter than 15 minutes, the reactions were not of first order.

The above results indicated that HA and FA from straw compost are quite capable of mobilizing insoluble P and other nutrients from both rock phosphates in significant amounts but their m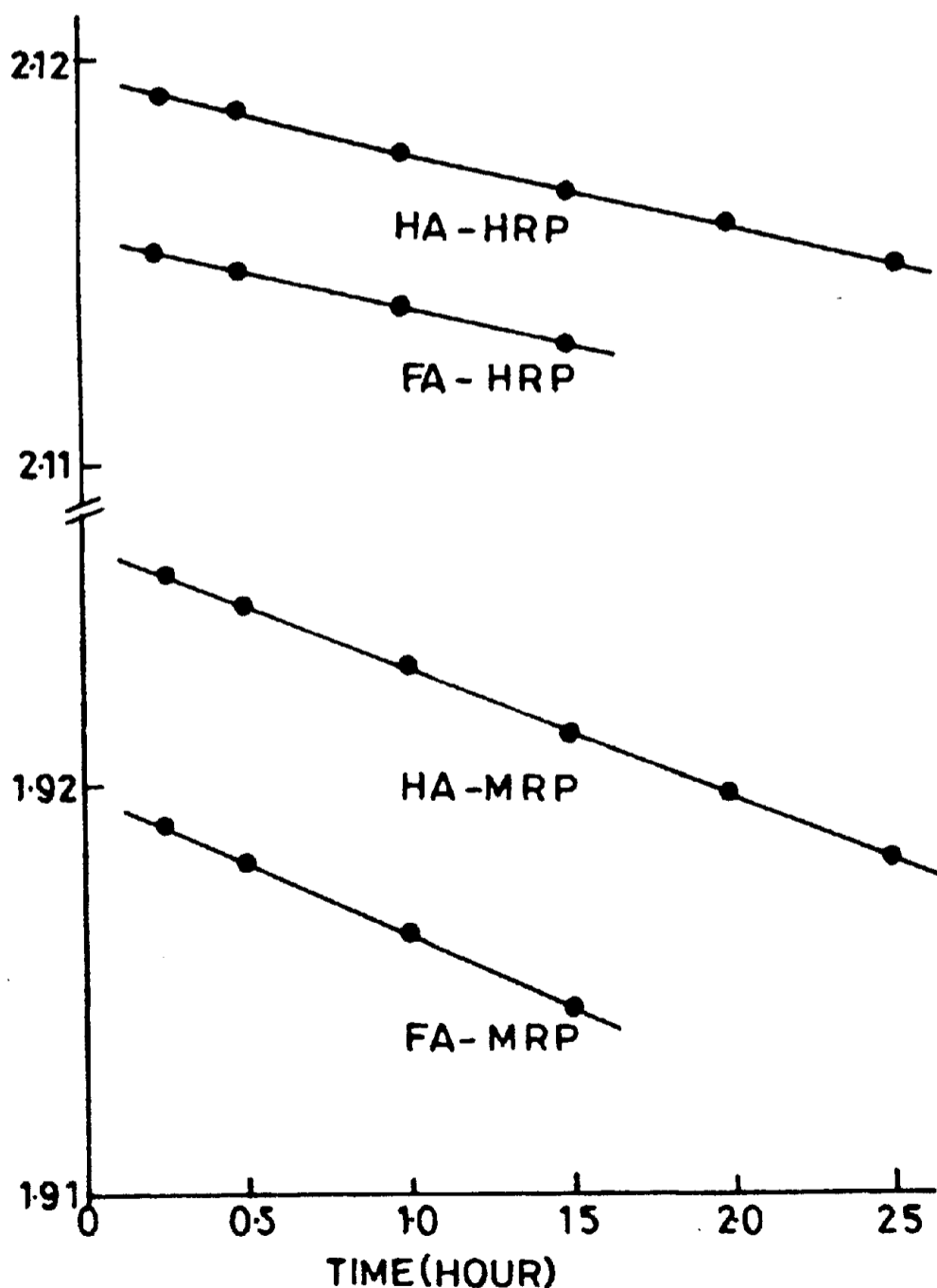aximum P-solubilizing capacity could only be achieved on maintaining 4:1 RP to HA and 6:1 RP to FA ratio. It was reported that during straw composting 25-35% organic matter humified into humic and fulvic acids with in 90-120 days of aerobic decomposition. The production of FA predominated over HA during initial stage of straw composting with rock phosphate (SINGH & AMBERGER, 1990).

In alkaline calcareous soils only 15-20% of applied soluble phosphates are utilized by plants and rest are precipitated with Ca converting into insoluble tricalcium phosphate and

FIG. 1. – Data of HA-and FA-Rock phospate interaction according to first order rate expressions.

finally into apatite rock at every time (SINGH & AMBERGER, 1995). These results assume a practical significance and suggest the potential of applying the unacidulated rack phosphate after composting with farm waste. This is not only non-polluting way of utilizing low grade rock phosphate but also increases the efficiency of saluble phosphate by restricting them from reprecipitation.

TABLE 4. – *The linear equation, Coefficient of correlation and rates of reaction of RP and HA/FA interaction.*

Interactions	Equation	r^2	Rate of reaction (K) $(mg\ P\ g^{-1}\ RP\ h^{-1})$
HA-MP	$\log C = -0.003t + 1.926$	0.994	0.007
HA-HP	$\log C = -0.002t + 2.112$	0.992	0.004
FA-MP	$\log C = -0.004t + 1.920$	0.999	0.008
FA-HP	$\log C = -0.002t + 2.115$	0.975	0.005

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SUMMMARY. – The influence of humic (HA) and fulvic acids (FA) from wheat straw compost on the solubilization of Mussooriephos (MP) and Hyperphos (HP) was studied. Solubilization of P from both rock phosphates (RP) increased up to 4:1, RP to HA ratio and 6:1, RP to FA ratio and thereafter decreased drastically, becoming negligible when pH of the equilibrium reached 7.35 on increasing the ratios. P solubility from HP was higher at lower ratios in comparison to MP. Fulvic acids had 80% higher P solubilizing capacity than humic acids.

The kinetic data indicated that the reaction was of first order and it was completed within 2.5 and 1.5 h respectively, for humic and fulvic acids.