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EFFECT OF ENRICHED STARCH PHOSPHATE AND CARBAMATE AS NATURAL FOLIAR FERTILIZERS ON YIELD AND MINERAL CONTENT OF SORGHUM

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Abstract

This study included two experiments; the 1st was conducted in the laboratory to find out the optimum conditions to prepare a natural organic foliar fertilizer (containing N, P, K, Fe, Mn and Zn) using corn starch as a carrier after certain modifications in starch properties and enriching it with the above-mentioned elements. The 2nd experiment was carried out in the greenhouse (pot experiment) to evaluate this foliar fertilizer at two levels (which referred as blends A and B) on the growth, yield and mineral content of sorghum plants, using alluvial, calcareous and sandy soils.

The obtained results revealed that :

1. The optimum laboratory conditions to reach the desired properties of the foliar fertilizer (containing appreciable amounts of total N and P in addition to the highest solubility percent in water) were when 100 g of corn starch was heated at 150°C for two hrs, with 5 ml., conc. phosphoric acid + 7.5 g urea.
2. Any deviation from the above-mentioned conditions led to a low water solubility of the foliar fertilizer (this property is considered one of the main properties of any foliar fertilizer).
3. Both of the two tested levels of this foliar fertilizer namely; blend A and blend B, (whereas blend B is two folds of the micronutrients content) recorded pronounced increases in dry weight., macro and micronutrients contents of sorghum plants in the three different soils over the control treatment.
4. The highest positive effects on growth, dry weight, along with macro and micronutrients contents were obtained in case of the interaction between alluvial soil and the highest level of this fertilizer (blend B).
5. The favorable effects of the treatments were in the order: blend B> blend A> control, whereas the sequence of soils was alluvial> calcareous> sandy.

The study alluded to the importance of using natural fertilizers as could as possible, considering human health must be in the first class.

INTRODUCTION

No doubt, the world's overpopulation that happened within the end of the twentieth century has resulted in a wide gab between production and consumption of most of the cereals and field crops. Increasing the cultivated area or intensifying crop cultivation to face or to fill this gab led to the use of huge amounts of chemical fertilizers which are not only so expensive but also do as agroecosystems pollutants. Thus, the current trend is to reduce the full dependence on mineral fertilizers and keep a high productivity in the meantime. Using macro- and micro-nutrients as foliar application may take part in decreasing these hazardous effects, as the use of such fertilizers will reduce the big losses that happen in case of soil application, and accordingly reduce the pollution of the environment.

In the last few decades, many investigators have used several and different kinds of foliar fertilizers and the pronounced effect of these fertilizers on the productivity of various crops has been known and needs no explanation, since it has been repeatedly reported in several literature.

Numerous investigators such as Stevenson and Ardakani (1972) and Roy *et al.* (1981) have indicated the efficiency of using several organic carriers either natural or synthetic; e.g. EDTA, EDDHA, humates as well as fulvic, amino and organic acids, lgnin-sulfonates and poly flavonoides. All these compounds are natural except the former two compounds while the latter two compounds are wood by-products in paper industry. Whenever the carriers were of natural origin it would be better and more safe than the synthetic ones from the environmental point of view.

Several attempts have been done by many investigators to modify the physical and chemical characteristics of native starch in order to promote its utilization for industrial purpose (paper, textile, food, adhesives, ...etc). Among these modifications is the estrification of starch using H_3PO_4 and other phosphate salts (Rutenberg and Solarek, 1984 and Waly *et al.*,1994). Also, Whistler *et al.* (1984) used H_3PO_4 in combination with urea as a promoter to increase the reaction (at 110-160°C) to prepare starch phosphate and starch carbamate. The former is considered one of the most important starch derivatives due to its wide applications as mentioned above in different industries.

Accordingly, the aim of the present study is to investigate the possibility of preparing soluble starch phosphate (St-P) and starch carbamate (St-C) using native corn starch plus orthophosphoric acid in the presence of urea to get a natural foliar fertilizer (after enriching with some essential elements) and then evaluating the efficiency of this fertilizer on growth (yield) and mineral content of sorghum plants through a pot experimental trial using alluvial, calcareous and sandy soils collected from different sites of Egypt.

MATERIALS AND METHODS

This study includes two stages; the first is to prepare the core materials (starch-phosphate; St-P & starch carbamate; St-C) on which the macro element potassium and some micronutrients are impregnated. The second stage is testing or evaluating the efficiency of these materials after impregnation as a foliar fertilizer on the growth, yield and mineral content of sorghum plants through a pot experiment trial using alluvial, calcareous and sandy soils collected from Giza Exp. St., Nubaria and Ismailia, respectively.

Laboratory preparation of starch phosphate and starch carbamate :

The theory or the idea of this reaction is based on the modification of the physical and chemical characteristics of native starch through estrification process by using phosphoric acid in the presence of urea as a promoter or a catalyst material. The suggested equation for the reaction may be represented as follows :

$$\underset{\text{Starch}}{\text{St-OH}} + \underset{\text{Phosphoric acid}}{\text{HO-}\overset{\overset{O}{\|}}{\text{P}}\text{(OH)}_2} \xrightarrow{\text{H}_2\text{N-}\overset{\overset{O}{\|}}{\text{C}}\text{-NH}_2} \underset{\underset{\text{(St-P)}}{\text{Starch phosphate}}}{\text{St-O-}\overset{\overset{O}{\|}}{\text{P}}\text{(OH)}_2} + \underset{\underset{\text{(St-C)}}{\text{Starch carbamate}}}{\text{St-O-}\overset{\overset{O}{\|}}{\text{C}}\text{-NH}_2}$$

Several preliminary laboratory attempts were carried out to find out the proper reaction conditions (i.e., temperature, duration, and reactants concentration) to prepare St-P & St-C, the materials which will be intended to be used as a foliar fertilizer (after enriching with micronutrients and potassium element). A constant weight of corn starch (100 g) was mixed with different volumes; 3, 4, 5 and 6 mls, of conc. phosphoric acid and different quantities, 2.5, 5, 7.5 and 10 g; of urea. The mixtures were heated in an electrical oven for different times; 1, 1.5, 2 and 2.5 hr., at various temperatures; 120, 130, 140 and 150°C. Table 1 shows all the conducted attempts of starch estrification (sixteen attempts including the four factors under study). Chemical testing to check the reaction progress was simultaneously performed during all these attempts to find out the optimum reaction conditions which lead to the desired specifications of these compounds, i.e. maximum N and P contents and maximum solubility% in water. High solubility% is considered an advantage in preparing this foliar fertilizer. It was found from Table 2, that the suitable conditions and concentrations were, 100 g corn starch + 7.5 g urea (46% N) + 5 ml conc., phosphoric acid (85%); the mixture was heated at 150°C in an oven for 2 hrs. The resultant powder of St-P and St-C was analyzed for detecting P and N contents (the two elements are present in the two starch compounds, respectively and are considered essential elements in plant nutrition). Nitrogen (N) and phosphorus(P) contents were determined by standard procedures of (A.O.A.C, 1990). Solubility% of the powder (in water) was determined according to Schoch (1964). The powder was kept for the following steps (for impregnation with some nutrient elements; K, Fe, Zn and Mn).

Impregnation of the powder with some nutritive elements :

Micro elements including Zn, Mn, and Fe (in the form of sulfate) and potassium sulfate were mixed thoroughly with St-P & St-C powders as follows:

1. The powder + 2% of each element (Fe, Zn and Mn) + 5% potassium (K); this mixture is referred as blend (A).

2. The powder + 4% of each element (Fe, Zn and Mn) + 5% potassium (K); this mixture is referred as blend (B).

All the nutrients were added on elemental basis in the form of sulfate salts. Blends (A) and (B) were kept to be evaluated later for their efficiencies as foliar fertilizer on sorghum plants in a greenhouse experiment.

Greenhouse experiment :

Pot experiment trial was conducted at Giza Exp. St., using alluvial, calcareous and sandy soils collected from Giza Exp. St., Nubaria and Ismailia locations, respectively. Sorghum seeds (H. 104) were sown in 20 kg soil/pot. The experiment was carried out on the 1^{st} of May 2000. Before sowing, each pot received superphosphate and potassium sulfate at the rates of 15 kg P_2O_5 and 24 kg K_2O/fed., 30 kg P_2O_5 and 24 kg K_2O/fed., and 30 kg P_2O_5 and 48 kg K_2O/fed. for the three above-mentioned soils, respectively. N was applied as ammonium sulfate at the rate of 80 kg, 100 kg and 110 kg/fed. for the three soils, respectively. It was applied in three equal doses, after thinning, after the 1^{st} cut and after the 2^{nd} cut. Six plants/pot were left after thinning. Plants were cut 3 times, the 1^{st} cut was after 40 days from sowing, the second after 40 days from the 1^{st} cut and the 3^{rd} was after 30 days from the 2^{nd} cut.

The averages of total yield (dry wt., as g/pot) and mineral content (N, P and K as g/pot, Fe, Zn and Mn as mg/pot) of the three cuts of sorghum plants were statistically analyzed according to Snedecor and Cochran (1980). Total N and P in plant samples were determined by standard procedure of A.O.A.C (1990). K was determined using the Flame photometer. The Atomic Absorption Spectrophotometer was used for micronutrients determination. Soil samples were collected before planting and were analyzed to determine physical and chemical properties according to Richards (1969). The soils are characterized by EC: 0.99, 0.84, 0.43 dS/m; pH: 7.91, 7.8, 7.1; O.M%: 2.25, 2.1, 0.5; their contents of available elements in ppm are N: 15, 10, 10; P: 36.0, 22.1, 7.0, K; 726, 653, 113; Fe: 6.8, 3.4, 3.3; Zn: 2.6, 2.2, 1.2 and Mn: 3.2, 2.06, 1.4; respectively for alluvial, calcareous and sandy soils, respectively.

The greenhouse experiment included three treatments as follows:

1. Control (no foliar application), used as a check treatment.
2. Spraying plants with blend (A) solution (4 gm of blend A powder/liter of water).
3. Spraying plants with blend (B) solution (4 gm of blend B powder/liter of water).

Each treatment was replicated four times. Plants were sprayed three times at 21 days from sowing date, two weeks after the 1^{st} cut and two weeks after the 2^{nd} cut.

RESULTS AND DISCUSSION

1. Effect of reaction conditions on the laboratory preparation of St-P & St-C :

As the main objective of this work is to investigate the possibility to prepare high soluble (if not complete soluble) starch phosphate and starch carbamate products (used as a natural and environmental safe foliar fertilizer) using H_3PO_4 (as a source of phosphorus) in the presence of urea (as a source of nitrogen) and to accelerate the reaction between starch and phosphoric acid. Thus to accomplish this objective, the effect of both reactants concentrations (H_3PO_4 and urea) as well as reaction time and temperature was studied.

Data presented in Table 1, illustrate all the laboratory attempts to find out the proper reaction conditions, taking in consideration certain properties that should be present in the products to be suitable as a foliar fertilizer. Among these properties, they should contain higher contents of both nitrogen (N) and phosphorus (P), as well as high solubility% in water, taking in consideration that reaching the highest contents of both elements should not be at the expense of the solubility% of these products. From the results shown in Table 2, it was found that the appropriate or optimum conditions to reach the desired properties were when 100 g of starch heated at 150°C for two hr., with 5 ml. conc. H_3PO_4 + 7.5 g urea. Under these conditions, the products contained appreciable amounts of total N (1.88%), total P (0.138%) and the highest solubility percent (99.5%). Although using more urea (10 g) led to the highest N (2.23%) and P (0.145%) content but not the highest solubility% (87%). So increasing urea above 7.5 g, will not fulfil the target of preparing high soluble foliar fertilizer. In the same respect, several authors have prepared starch phosphate ester by using different phosphate salts and H_3PO_4 (Chong-Tai Kim *et al.*, 1999 and Waly *et al.*, 1994). Rutenberg and Solarek (1984) stated that using urea in the phosphorylation process (when H_3PO_4 was used) accelerated the reaction. They added that urea used in this reaction was also incorporated in the phosphate ester to form starch phosphate and starch carbamate as shown in the equation. In the same respect, Alexander (1984) also found that using 2-3% urea and 1-6% Na-tripolyphosphate produced starch phosphate and starch carbamate containing <0.3% bound P and carbamate groups containing 1.3-

Table 1. Laboratory attempts* to find out the optimum conditions to prepare starch derivatives (St-P[1] and St-C[2]) from corn starch**.

Treatment	Temperature °C	Time hr.	Phosphoric acid (ml)	Urea (gm)
	Variable			
1	120	2.0	5	7.5
2	130	2.0	5	7.5
3	140	2.0	5	7.5
4	150	2.0	5	7.5
		Variable		
5	150	1.0	5	7.5
6	150	1.5	5	7.5
7	150	2.0	5	7.5
8	150	2.5	5	7.5
			Variable	
9	150	2.0	3	7.5
10	150	2.0	4	7.5
11	150	2.0	5	7.5
12	150	2.0	6	7.5
				Variable
13	150	2.0	5	2.5
14	150	2.0	5	5.0
15	150	2.0	5	7.5
16	150	2.0	5	10.0

* Sixteen attempts (or treatments) including four variable factors (temperature, reaction time, reactants concentrations which are phosphoric acid and urea).

** A constant weight of corn starch (100 g) was used with each treatment. Corn starch was provided by the Egyptian Company for Starch and Glucose Manufacturing.

(1) Starch-phosphate. (2) Starch-Carbamate.

Table 2. Effect of reaction conditions (temperature, time, phosphoric acid and urea) on the properties* of the laboratory prepared starch phosphate (St-P) and starch carbamate (St-C).

Serial No.	Reaction conditions		Properties		
			Solubility %	P %	N %
	Temperature (°C)				
1		120	60.60	0.104	0.95
2		130	80.30	0.106	1.63
3		140	86.50	0.120	1.78
4		150	99.50	0.138	1.88
	Time (hr.)				
5		1.0	73.00	0.091	1.19
6		1.5	91.62	0.127	1.67
7		2.0	99.50	0.138	1.88
8		2.5	90.50	0.139	1.72
	Phosphoric acid (ml)	3	83.30	0.127	1.19
9		4	94.50	0.131	1.42
10		5	99.50	0.138	1.88
11		6	90.50	0.130	1.72
12					
	Urea (gm)				
13		2.5	84.10	0.101	0.98
14		5.0	96.60	0.124	1.25
15		7.5	99.50	0.138	1.88
16		10.0	87.00	0.145	2.23

* The desired properties are high solubility % as well as high contents of both N and P elements. So the optimum conditions obtained from this table to reach these desired properties were when 100 gm of corn starch heated at 150 °C for two hrs, with 5 mls, conc. phosphoric acid + 7.5 gm urea.

1.7% N. As for the effect of the reactants concentration on the rate of reaction, Waly *et al.* (1994) stated that increasing H_3PO_4 and urea concentrations led to an increase in the phosphorylation reaction; they ascribed this effect to the proximity of these reactants to the OH-groups in starch molecules.

As for the other two factors affecting the reaction process, i.e., temperature and time of reaction, the obtainable data (Table 2) revealed that150°C for 2 hrs, ensured appreciable amounts of N and P in addition to maintaining the highest solubility (99.5%) of the products under study. Using temperature below 150°C and reaction time below or above 2 hrs, has decreased solubility%. These results are in agreement with the data obtained by Khalil *et al.* (1994) and Waly *et al.* (1994); the latter authors also stated that the higher temperature may favour the reaction through starch degradation and decomposition of urea. Rutenberg and Solarek (1984) stated that extending heat treatment from 1 to 2 hrs, led to increasing (P) content from 0.37 to 0.47%.

2. Effect of St-P and St-C (enriched with K and some micronutrients) on yield and mineral contents of sorghum plants :

Tables 3 and 4 illustrate data representing yield as indexed by dry wt., macro- and micro-nutrients contents of sorghum plants grown on three different soils (alluvial, calcareous and sandy) as influenced by foliar spraying with the enriched starch compounds at two levels as represented by blend (A) and blend (B).

Data indicated that the highest positive effects on growth (dry wt.), macro- and micro-nutrients content (P, K, Fe, Mn and Zn) were obtained in case of the interaction (a x b), i.e. between the alluvial soil and blend B treatment {i.e., when sorghum plant was grown in alluvial soil and foliar sprayed with blend (B)}. The recorded values were 89.8, 0.21, 4.333 (g/pot), ≅ 22.87, 5.55 and ≅ 4.29 (mg/pot), respectively. The aforementioned data were quite expected for two reasons, the first is that blend (B) (used as a foliar application) is more rich in micronutrients (4% of each Fe, Mn and Zn elements) than blend (A) (contains only 2% of each element). The second reason is that the alluvial soil is more fertile and rich in those elements than the other two soils. Also, all the data (dry wt., N, P, K and micronutrients) belonging to blend B treatment recorded the highest significant values as compared with blend A and the control treat-

Table 3. Yield and macronutrients content of sorghum plants (grown on three different soil types) as influenced by foliar spraying with starch drivatives (enriched with potassium and some micronutrients).

	Yield (dry Wt. g/pot)				Macronutrients contents (g/pot)											
					N				P				K			
Soil type / Treatments	Alluvial	Calcareous	Sandy	Mean (b)	Alluvial	Calcareous	Sandy	Mean (b)	Alluvial	Calcareous	Sandy	Mean (b)	Alluvial	Calcareous	Sandy	Mean (b)
Control	83.87	54.30	38.37	58.84	1.67	0.97	0.99	1.21	0.18	0.13	0.09	0.13	4.17	2.97	1.72	2.95
Spraying with Blend (A)	85.23	57.67	43.93	62.28	1.59	1.09	1.07	1.25	0.19	0.14	0.12	0.15	4.19	3.22	1.83	3.08
Spraying with Blend (B)	89.80	66.10	44.57	66.82	1.64	1.44	1.07	1.39	0.21	0.17	0.10	0.16	4.33	3.48	2.05	3.29
Mean (a)	86.30	59.35	42.29	62.65	1.63	1.17	1.04	1.28	0.19	0.15	0.11	0.15	4.23	3.22	1.87	3.11
L.S.D. at 0.05 level																
(a) Soil	1.61				0.05				0.09				0.05			
(b) Treatment	2.08				0.07				0.11				0.07			
(axb) Soil x Treatment	3.60				0.12				0.20				0.12			
L.S.D. at 0.01 level																
(a) Soil	2.16				0.072				0.12				0.07			
(b) Treatment	2.80				0.093				0.15				0.09			
(axb) Soil x Treatment	4.85				0.160				0.26				0.16			

Table 4. Micronutrients content of sorghum plants (grown on three different soil types) as influenced by foliar spraying with starch derivatives (enriched with potassium and some micronutrients).

	Micronutrients contents (g/pot)											
	Fe				Mn				Zn			
Treatments \ Soil type	Alluvial	Calcareous	Sandy	Mean (b)	Alluvial	Calcareous	Sandy	Mean (b)	Alluvial	Calcareous	Sandy	Mean (b)
Control	20.13	14.36	11.70	15.39	4.27	2.75	1.75	2.92	2.29	1.95	1.55	1.93
Spraying with Blend (A)	21.57	15.40	12.77	16.58	4.85	3.29	2.27	3.47	2.62	2.12	2.02	2.25
Spraying with Blend (B)	22.87	19.13	13.57	18.52	5.55	4.54	2.62	4.24	4.29	3.29	2.07	3.22
Mean (a)	21.52	16.30	12.68	16.83	4.89	3.53	2.22	3.55	3.07	2.45	1.88	2.47
L.S.D. at 0.05 level												
(a) Soil	0.78				0.24				0.16			
(b) Treatment	1.00				0.31				0.21			
(axb) Soil x Treatment	1.75				0.54				0.36			
L.S.D. at 0.01 level												
(a) Soil	1.05				0.33				0.22			
(b) Treatment	1.36				0.42				0.28			
(axb) Soil x Treatment	2.35				0.72				0.48			

ments. The corresponding values belonging to blend B treatment were 66.82, 1.39, 0.16 and 3.29 g/pot for dry wt., N, P and K and 18.52, 4.24 and 3.22 mg/pot for Fe, Mn and Zn, respectively. From the tables, it could be noted that the favorable effects of treatments were in the order of; blend B> blend A> control, whereas the sequence of soils effect is alluvial> calcareous> sandy. As for the response to the foliar treatments, the trend was according to the following sequence; calcareous> sandy> alluvial.

The pronounced effect of blend B (due to its higher content in elements) on the increase in yield (dry wt.) as well as the increase in uptake of macro- and micronutrients by sorghum plants was quite expected and well known and even needs no explanations, although many authors (Mortvedt and Giordano, 1971; Badr *et al.*, 1991 and El-Fouly and Fawzi, 1996) have reported the close relationship and interaction among the essential elements (either macro- or micro-nutrients) in several bioprocesses and then building up dry matter of most crops and thus the total yield of them.

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تأثير فوسفات وكربامات النشا بعد إثرائهم بالعناصر الغذائية كسماد ورقى طبيعى على المحصول والمحتوى العنصرى لنبات الذرة الرفيعة

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أقيمت تجربتان الأولى منهما تجربة معملية أجريت بالمعمل لمعرفة الظروف المثلى لتحضير وتجهيز سماد ورقى عضوى طبيعى باستخدام نشا الذرة بعد تحوير بعض الصفات الطبيعية للنشا واستخدامه كحامل لبعض العناصر الغذائية الكبرى والصغرى (مثل النيتروجين والفوسفور والبوتاسيوم والحديد والمنجنيز والزنك). وكانت أهم النتائج المتحصل عليها كما يلى :

١- أدت التجارب المعملية العديدة للتوصل لأمثل الظروف للحصول على تركيبة لسماد ورقى على درجة عالية من الذوبان فى الماء (وهى من أهم الصفات المرغوبة فى الأسمدة الورقية) وفى نفس الوقت المحافظة على احتواء هذا السماد على نسب من العناصر الغذائية مناسبة - وكانت أمثل الظروف لتحضير هذا السماد هو عند استخدام ١٠٠ جرام من نشا الذرة + حجم ٥ ملليلتر من حمض الفوسفوريك المركز + ٧,٥ جرام يوريا وتسخين المخلوط لمدة ساعتين فى فرن على درجة حرارة ١٥٠° م.

٢- وجد أن أى حيود أو اختلاف عن الظروف السابقة من تركيزات للمواد الداخلة فى التفاعل أو الحرارة أو زمن التفاعل تؤدى إلى نقصان نسبة الذوبان لهذا السماد بدرجة كبيرة وكذلك تؤثر سلباً على نسب العناصر الداخلة فى تركيب هذا السماد.

أما التجربة الثانية فقد نفذت فى الصوبة (تجربة أصص) وذلك بغرض تقييم هذا السماد باستخدام تركيزين منه (تركيز أ، تركيز ب). أحتوى التركيز (أ) على نصف التركيز الثانى (ب) من محتوى العناصر الصغرى وذلك لتقييم أثر هذا السماد على نمو ومحصول ومحتوى العناصر الغذائية فى نباتات الذرة الرفيعة المزروعة فى ثلاثة أنواع من الأراضى المصرية (طينية - جيرية - رملية). وكانت أهم النتائج المتحصل عليها كما يلى :

١- وجد أن الرش بالسماد الورقى تحت الأختبار (بتركيزيه أ، ب) أدى إلى زيادات ملحوظة فى قيم محصول المادة الجافة والمحتوى العنصرى (من النيتروجين، الفوسفور، البوتاسيوم، الحديد، المنجنيز، الزنك) فى نباتات الذرة الرفيعة المزروعة فى الثلاث أراضى المذكورة وكانت معاملة المقارنة هى أقل القيم.

٢- سجلت المعاملة التفاعلية بين التربة الطينية ومعاملة الرش بالتركيز العالى ب أعلى قيم من محصول المادة الجافة والمحتوى العنصرى لجميع العناصر الغذائية السابقة.

٣- كانت أفضلية النتائج على النحو التالى:

الرش بالسماد الورقى تركيز ب> نفس السماد بتركيز أ> معاملة المقارنة. وبالنسبة للأراضى

تحت الدراسة كانت القيم كما يلى طينية > جيرية > رملية. وقد سجلت الاستجابة لمعاملات الرش الترتيب التالى : جيرية > رملية > طينية.

وقد ألحت الدراسة إلى أهمية وجوب استخدام الأسمدة الطبيعية عن نظيراتها المخلقة بقدر الإمكان آخذاً فى الأعتبار وضع صحة الإنسان فى المقام الأول.