

Development of a Multi-Component Fertilizing Hydrogel with Relevant Techno-Economic Indicators

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Abstract: In view of the current national reclamation programs, a significant increase in fertilizer demand is predicted. The ideal fertilizer should be able to provide essential nutrients and preferably with reasonable water holding capacity. Further, it should be eco-friendly and affordable. This paper presents the experimental investigations conducted for hydrogel preparation, characterization and testing. The new process design features of a multi-component fertilizing hydrogel with slow release characteristics are outlined. The developed hydrogel blend (HESRF) can provide essential plant nutrients including nitrogen, phosphorous, potassium and zinc as well as the organic matrix which acts as a soil conditioner. Preliminary agriculture testing confirmed the fertilizing value of HESRF. The prepared fertilizing base (ESRF) contained 65-70% starch, 28-33% urea and 2% of other ingredients (zinc, potassium and phosphorous). It was also found that the beneficial effect of HESRF is obvious on faba bean and wheat crops. For instance, the grain yield for wheat reflects 89% and 116% increase using ESRF and HESRF respectively as compared with the normal fertilizing treatments. Comparable seed yields for faba bean are 43% and 78% respectively. Preliminary cost estimates were conducted for a small scale industrial production facility (10 ton /day). The estimated cost of HESRF is about 770 \$/ton. It is perceived that the economics of the production could be significantly improved if cheap substrates are used (e.g. waste food grains and other polysaccharide sources).

Key words: Slow release fertilizer • Hydrogel • Starch • Agriculture • Economics

INTRODUCTION

Arid land reclamation program in Egypt is a central component in the Egyptian social and economic development strategies in the last decades. The success of this program is mandatory to secure food supplies and avail intensive job opportunities. Other targets of reclamation program are to establish new agro-industrial complexes to decrease population and development pressures in the old Nile valley. With the current degradation of significant agricultural areas in the valley, to satisfy demand for housing and urban services, it is necessary to develop new reclaimed lands. The main challenges for most land reclamation projects are the availability and accessibility of funding, water, energy and fertilizers. Excessive consumption of fertilizers is thus a challenge that should be mitigated by the new land owners and developers.

Advanced chemical technologies enabled commercial production of new soil conditioners and slow release fertilizers that match the requirements of desert land reclamation [1-3]. High swelling hydrogels (HSG) based on natural and synthetic polymers are characterized by high water retention capacity of about 50-1000 gram of water per gram of dry hydrogel [4-6]. The immediate impact is water conservation enabling sustainable water inputs to the growing plant under prevailing arid conditions. Improving sandy soils is also an additional benefit related to the application of HSG to desert land [7]. Optimization of fertilizer consumption has been realized through the development of effective slow release fertilizers (e.g. slow release urea) that extends availability of the added nutrients via minimizing losses with water to underground soils. Realizing the strategic importance of those developed soil conditioners and slow release fertilizers, the development of HSG has been investigated

in previous work [4-6,8-10]. Corn and potato starches were used as substrates for grafting with acrylonitrile using Fenton redox system. The product was characterized by moderate water swelling capacity (60 g/g) [8]. Ceric catalyst showed higher swelling capacity for the produced hydrogel (up to 400 g/g) [9,10] but, its use for agricultural purposes is prohibitive due to high catalyst cost. Other HSG based on synthetic polymeric substrate have been reported based on polyvinyl alcohol [4,6]. Slow release fertilizer based on corn starch /acrylonitrile grafting with formaldehyde and phosphate as cross linkers have been reported by Production [9] and Talaat *et al.* [10]. The produced gel had relatively low swelling characteristics with significant phosphate and nitrogen content. Urea form which is a condensation product between urea and formaldehyde has been reported to be a potential slow release fertilizers [11]. Urea coated with copolymer of acrylamide/ tetra ethylene glycol has been reported to have good slow release property [12]. The main objective of this paper is the development of cost-effective gels through incorporation of low cost raw materials and tailoring manufacturing process to cope with the characteristics of small to medium scale companies.

Research Rationale: Techno-economic studies indicated the need for affordable gels to improve farming economics. Further, land application may be simple and cost effective if other fertilizing inputs are incorporated within the matrix of the gel. Thus, the new development targets preparation of a rational blend of HSG and SRF. The latter type will be also enriched with potassium and zinc salts (ESRF). The target blend manufacturing strategies should accommodate incorporation of low cost materials (waste starch or off specs food ingredients). Also, ESRF should be manufactured according to the prevailing limitations and resources of small and medium scale industries. This later consideration is vital to permit expanded manufacturing base. More over, blending of HSG with ESRF should yield fertilizing compound with moderate water retaining capacity (HESRF).

MATERIALS AND METHODS

Materials: Raw materials employed for the preparation of HSG comprise corn high grade starch obtained from Sigma- Aldrich Chemie, Germany, acrylonitrile (99 %, inhibited with 35–45 mg/l monomethyl ether hydroquinone) from Sisco Research Laboratories PVT. Ltd- India, laboratory grade. Hydrogen peroxide

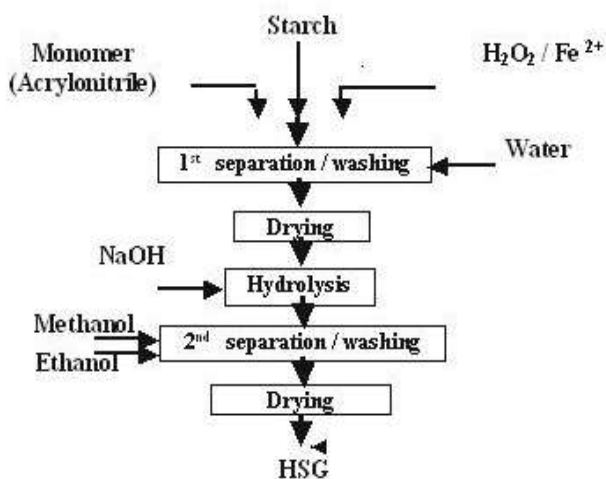


Fig. 1: Block diagram for the production of the high swelling hydrogel (HSG)

(50%w/v), methanol and ethanol were obtained from Adwic, Egypt; laboratory grade ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was supplied by S.D. Fine Chem. Ltd, laboratory grade and acetic acid was supplied by United Company for Chem. & Med. Prep., Egypt. Sodium hydroxide beads were supplied by modern Lab. Egypt. ESRF comprises commercial corn starch, urea, phosphorous (P), potassium (K) and zinc (Zn) salts. Limited agricultural laboratory experiments were conducted using small pots for plantation of faba bean cultivate Giza- Blanka and wheat cultivate Sakha – 69. Faba bean seeds and wheat grains were obtained from Agriculture Research Centre, Ministry of Agriculture- Egypt.

Methods: The adopted methodological milestones for preparation and testing of the developed HESRF comprises:

- Preparation of ESRF through sequential addition and mixing of different ingredients followed by controlled drying and size reduction procedures.
- Preparation of HSG according to the simplified scheme in Figure 1.
- Blending of HSG and ESRF at the point of use.
- Limited in house agricultural tests.
- Preliminary cost analysis.

Preparation of HSG: HSG was prepared in two steps including grafting of starch with acrylonitrile followed by saponification of the produced graft and alcohol separation of HSG.

Grafting Polymerization: One hundred grams of washed starch with ethyl alcohol, 140 gm of acrylonitrile (AN), 5 ml of non ionic surfactant were added with distilled water (liquor ratio 1:10). The mixture was mixed by a magnetic stirrer and sparged with a slow stream of nitrogen. H_2O_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solutions were injected to the reaction vessel to begin the grafting process with a weight ratio of 6 for H_2O_2 : $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The reaction time was 30 minutes at room temperature followed by another 30 minutes at 30°C then 15 minutes at 35°C and additional 15 minutes at 40°C . The product was filtered, washed by distilled water and then dried at room temperature.

Alkaline Saponification: A suspension of poly AN grafted starch in 0.7 N NaOH (liquor ratio 1/9, w/v) was introduced in a reflux system and mixed well. The system was then placed in a water bath. Saponification was maintained for an hour at 95°C till complete saponification (the colour changes from deep red to light brown). The mixture was cooled then dispersed in methanol (1/6, w/v). The precipitate was washed with slightly acidified ethanol (ethanol with few drops of acetic acid until $\text{pH}=8$), then filtered and dried at 60°C for 3 hours.

Preparation of ESRF: The different ingredients of ESRF were added sequentially with good mixing. Sufficient time has been allocated for individual mixing steps to ensure thorough distribution of each fertilizing component. The minimum mixing time of the fertilizing paste is around 4 hours. Typical initial blend contains 65-70% starch, 28-33% urea and 2% of other ingredients (P, K and Zn). Drying has been undertaken on three stages: from 20°C to 60°C for 90 min then, from 60°C to 90°C for 60 min and finally from 90 to 110°C for 50 min. The obtained dry mass has been grounded and screened.

Preparation of the Fertilizing Hydrogel Blend (HESRF): Mixtures of HSG and ESRF are intimately mixed according to the design ratio prior to testing.

Characterization and Performance of HESRF

a - Chemical Compositions: For both ESRF and HSG, analysis of nitrogen content is determined according to Kjeldahl method. For ESRF, phosphorous was analysed using spectrophotometer (Perkins Elmer, model lambda 2) While, K and Zn were determined using an atomic absorption spectrophotometer (Perkins Elmer, model 1100B) [13].

b - Release Experiments: Release characteristics of hydrogel blends were determined by three experimental sets.

The First Set: Seven samples of 0.8 gm of ESRF in 100 ml distilled water.

The Second Set: Seven samples of the hydrogel blend each comprising 0.8 gm of ESRF and 0.2 gm of HSG in 100 ml distilled water.

The Third Set: Seven samples of the hydrogel blend each comprising 0.8 gm of ESRF and 0.2gm of HSG in 100 ml alkaline solution adjusted to $\text{pH}=8.5$ which simulates the soil pH in Egypt. For the first and the second sets, samples were taken daily for 9 successive days and for the third set, samples were taken daily through 26 days. Samples were analysed for determination of nitrogen (N), P, K and Zn [13].

c - Agricultural Assessments:

- The agricultural tests were conducted during the season of 2006 / 2007 at the experimental greenhouse of National Research Centre- Dokki- Giza to study the effect of the multi fertilizing hydrogel (HESRF) on the yield of faba bean and wheat plantation.
- The seeds and grains were selected for uniformity in size, shape and colour and sown in 50 cm diameter clay pots (20 Kg clay loam soil).
- Each pot received equal and adequate amount of water and fertilizers. Phosphorus as super phosphate was mixed with the soil before sowing for each pot.
- Ten seeds and /or grains were sown in each pot. Fifteen days after sowing, the seedlings were thinned to the most three uniform plants in each pot.

Three different treatments were applied starting 21 days after sowing as follows:

- Control (Normal treatment (NF)): (30 pots), 3 gm of nitrogen as ammonium sulphate were added in three applications at intervals of three weeks.
- Treatment with ESRF: (15 pots for faba bean and 15 pots for wheat).
- Treatment with HESRF: (15 pots for faba bean and 15 pots for wheat).

For each treatment, plant per pot representing five replicates was left for yield determination. The yield was harvested and weighed after complete drying

of pots. Both seed or grain yield/ plant, straw yield/plant and above ground biomass/ plant (i.e. seed or grains and straw yields) were determined. Other agriculture processes were performed according to the normal practice [14].

RESULTS AND DISCUSSIONS

Chemical Compositions: The chemical contents of the ESRF for N, P, K and Zn are: 14 %, 5.6 mg/g, 9 mg/g and 0.65 mg/g, respectively. Nitrogen content in HSG is about 2.1%.

Release Profile: The release profiles for the pre-mentioned components are depicted in Figures (2- 5).

Figure 2 shows the release profile for N and K from ESRF and HESRF in distilled water. N shows high release after 24 hours, followed by considerable reduction in N content. This may be attributed to the initial solubilization of nitrogenous compounds from the hydrogel-blend during the first day. Increasing the pH to 8.5, increases N release in the 12 days to a maximum of 500 mg/l (Figure 3). The reduction of nitrogen content with time could be attributed to urea dissociation under the experimental conditions to ammonia which volatilizes leading to a net nitrogen reduction [15]. The results indicate that HESRF has superior N release characteristics than ESRF. It is also noticed that for HESRF, increasing pH to 8.5 enhances N release. The results indicate also that a bout 86% of the potassium has diffused out of HESRF after about 8 days. On the contrary, almost all the potassium content has been released into the solution after 24 hours for ESRF. This reflects the regulating effect of the HESRF composition which may be attributed to potassium exchange with sodium in the hydrogel component. Further, increasing the pH to 8.5 manifests the same trend for HESRF (about 36% of the initial potassium content is still within the matrix after 26 days). The release profiles for phosphate and zinc in distilled water and alkaline solutions are presented in Figures 4 and 5, respectively. Almost about 100% and 78% of the phosphate content showed release after 48 hours into the alkaline solution and distilled water, respectively. The presence of hydrogel component slightly augments phosphate release. On the other hand, the release profile of zinc / HESRF depicts minimal release in both distilled water and the alkaline solution being about 9% and 5% of its initial content after 8 days, respectively. The regulating effect of the hydrogel component is manifested by the lower release of zinc by HESRF as compared to ESRF.

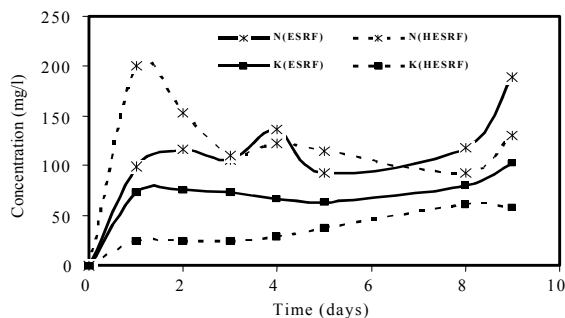


Fig. 2: Release profiles for N and K in distilled water (pH = 6.5) for the two fertilizing formulae

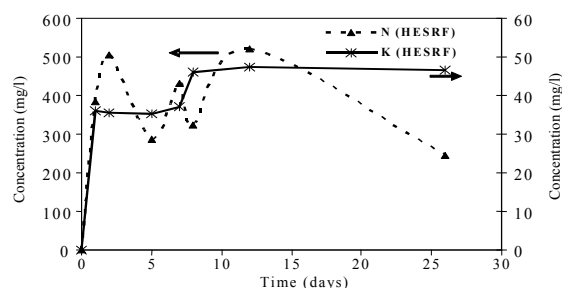


Fig. 3: Release profiles for N and K in alkaline solution (pH=8.5) for HESRF fertilizing formula

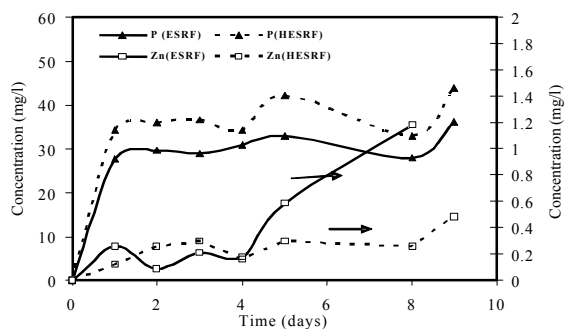


Fig. 4: Release profile for P and Zn in distilled water (pH=6.5) for the two fertilizing formula

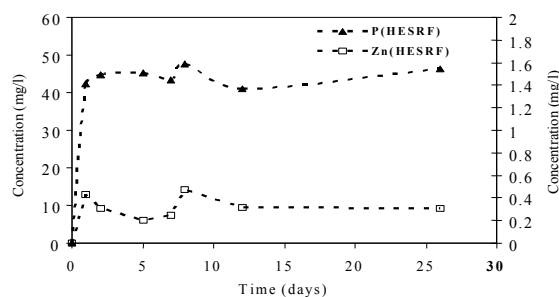


Fig. 5: Release profiles for P and Zn in alkaline solution (pH=8.5) for HESRF fertilizing formula

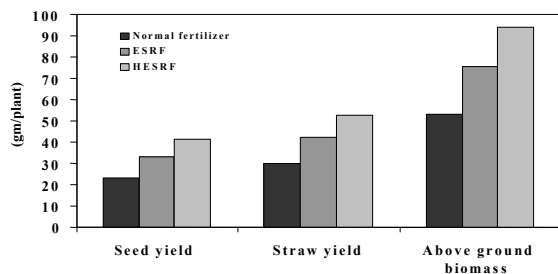


Fig. 6: Comparison of Faba bean plantation pot experiments

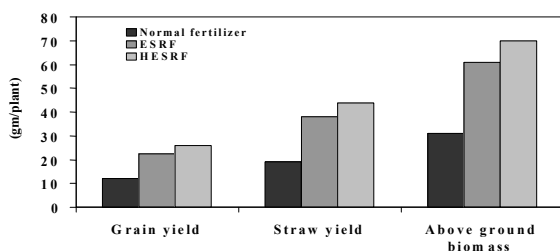


Fig. 7: Comparison of wheat plantation pot experiments

Crop Yield: Substantial improvement was achieved by the application of the newly developed fertilizers (ESRF &HESRF). Figures 6 and 7 compares the yield of seed / grain, straw and above ground biomass generated from pots treated with normal fertilizer (control), ESRF and HESRF for faba bean and wheat crops, respectively. For faba bean, the seed yields are 23, 33.2 and 41.4 gm/plant for the three fertilizing treatments, respectively. Comparable straw yield are 29.9, 42.2 and 52.6 gm/plant, respectively. The beneficial effect of HESRF formula is obvious on both crops. For instance, the grain yield for wheat reflects 89% and 116% increase using ESRF and HESRF, respectively as compared with the normal fertilizing treatments.

Financial Indicators and Implications on Farm Economics

Cost Estimates: The construction cost for small scale production units for HSG and ESRF each of 10 t/day production capacity were estimated based on updated cost data for equipment and basis listed in Table 1.

Table 1: Construction cost estimation of HSG and ESRF production (10 ton / day)

		Cost (\$1000)	
Item	Specification / basis	HSG	ESRF
I. Equipment Cost			
1- Grafting reactor	Stirred tank reactor, 1000L, SS316 with jacket and reflux condenser (installed power: 5.5 KW)	68	-
2- Homogenizer	Stirred tank SS304 1000L ribbon mixer and variable speed (7.5 KW)	-	90
3- Rotary filter (1)	Rotary vacuum filter, 10m ² area with vacuum pump and filter cake washing system (installed power: 7.5 KW)	80	-
4- Rotary filter (2)	Rotary vacuum filter, 8m ² filtration area with vacuum pump and filter cake washing system (installed power: 5.5 KW)	64	
5- Hydrolyser	Stirred tank reactor, 1500L, SS316 with heating & cooling jacket (installed power: 7.5 KW)	88	
6- Dryer (1)	Vacuum tray dryer with gas fuel burner, air fans and cyclone for dust collection, capacity 1ton dry solids/hr (installed power: 3KW).	107.2	
7- Dryer (2)	Vacuum tray dryer with gas fuel burner, air fans and cyclone for dust collection, capacity: 0.8 ton dry solids/hr (2.2 KW)		105
8- Tanks	SS 316 tanks	10.7	
9- Solvent recovery unit	Methanol recovery unit (250 liter/hr): distillation column, boiler with electric heater, condenser, reflux pumps and instrumentation, (installed power: 5.5 KW)	110	
10- Mill	Rotary knife disintegrator (250kg/hr), SS 304 (installed power: 11KW).	63	63
Subtotal (I)		590.9	258
II. Piping	10% of equipment cost	59.1	25.8
III. Electrical	8% of equipment cost	47.3	20.6
IV. Instrumentation and control	5% of equipment cost	29.5	12.9
V. Others (engineering, contingencies, etc...)	5% of equipment cost	29.5	12.9
Total construction cost		756.3	330.2

Table 2: Cost estimates basis for HSG and ESRF production (10 ton / day)

Cost item	Cost estimate basis	
	HSG (10 ton / day)	ESRF (10 ton / day)
*1. Operating cost		
1.1 Chemicals & Materials		
1-High grade corn starch	1800 t/yr at \$ 500/t.	-
2-Commercial corn starch	-	2000 t/yr at \$ 350/t.
3-Acrylonitrile	1800 t/yr at \$ 2500/t.	-
4-Urea	-	1000 t/yr at \$ 350/t.
5-Sodium hydroxide	50 t/yr at \$ 600/t.	-
6-Ferrous sulphate	50 t/yr at \$ 350/t.	-
7-Hydrogen peroxide (50%)	300 t/yr at \$ 1000/t.	-
8-Acetic acid	1.5 t/yr at \$ 1800/t.	-
9-Citric acid	-	30 t/yr at \$ 900/t.
10-Phosphoric acid (50%)	-	-15 t/yr at \$ 900/t.
11-Methanol**	500 t/yr at \$ 600/t.	-
12-Ethanol**	100 t/yr at \$ 1500/t.	-
13-Potassium and zinc salts	-	70 t/yr at \$ 800/t.
14-Water	60000 m ³ /yr at \$ 0.2/ m ³	6000 m ³ /yr at \$ 0.2/ m ³
1.2 Electricity	100 KWh/t at \$ 0.08/KW.h 3 % of equipment cost	60 KWh/t at \$ 0.08/KW.h
1.3 Maintenances		3 % of equipment cost
1.4 Labour	\$ 15/ t	\$ 10 / t
1.5 Others	10 % of total operating costs	10 % of total operating costs
2. Depreciation	Plant life,15 years, equal annual installments	Plant life,15 years, equal annual installments

*Daily production: 10 ton/day (annual working days, 300 days) ** Solvent loss = 5% of total solvent used.

Table 3: Production cost estimates for HSG and ESRF production (10 ton /day)

Cost item	Annual cost (\$1000/yr)	
	HSG (10 ton / day)	ESRF (10 ton / day)
1. Operating cost		
1.1 Chemicals & Materials	6212.2	1147.7
1.2 Electricity	24.0	14.4
1.3 Maintenances	17.7	7.8
1.4 Labour	45.0	30.0
1.5 Others	669.9	133.3
Total Operating cost	6998.8	1333.2
2. Depreciation	50.4	22.0
Total production cost	7049.2	1355.2
Cost per ton(\$/t)	2349.7	451.7

The construction costs for establishing production facilities of 10 t/day [16] are \$ 756,300 and \$ 330,200 for HSG and ESRF, respectively. The basis for production cost estimation is illustrated in Table 2. The production costs are estimated to be \$ 2349.7 and \$ 451.7 /t for HSG and ESRF respectively as shown in Table 3.

Implications on Farm Economics: Based on a small scale production facility for the HSG/ ESRF blend (HESRF),

with a conservative blending ratio of 1:5 (HSG/ESRF), the production cost of HESRF is estimated to be about \$ 770/t. Assuming a market selling price of \$ 900/t of HESRF, the application rate of HESRF is 120 kg/acre with an additional cost of \$ 108 /acre. This additional cost is compensated by the benefits due to increasing yield of seeds & straw as indicated by the agricultural tests.

CONCLUSIONS AND RECOMMENDATIONS

A newly fertilizing slow release blend (HESRF) has been developed by appropriate mixing of the newly developed ESRF and HSG. Preliminary agricultural experiments using in house pots showed an excess of seed/grain yield for faba and wheat crops by about 80% and 116%, respectively as compared to the normal fertilizing treatment. Slow release experiments manifested characteristics of slow release pattern for the developed fertilizing blend (HESRF) and HSG component seems to regulate zinc and potassium release probably through ion exchange component. The technical and financial aspects of production facilities for both HSG and ESRF are

presented to come up with a cost estimate for an applicable blend (HESRF) comprising of HSG and ESRF. The added cost due to the application of HESRF is about 108 \$/acre is surpassed by the benefits obtained through the increased crop yield. Additional R&D efforts are currently underway to optimize the production costs of both ESRF and HSG. Further, large scale agricultural application trials are currently planned to explore the cost/benefit pertinent to the application of the new fertilizing blend.

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