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Techno-economic investigation for production of innovative hydrogel as superabsorbent polymer.

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ABSTRACT

A comprehensive experimental study on pilot plant scale for production of an innovative hydrogel as super-absorbent polymer was previously investigated. Two types of hydrogel materials were produced in forms of powder and gel past, via three main processes: starch phosphorization, polymerization of a vinyl monomer onto the starch phosphate using either ammonium persulphate and sodium bisulphite (APS/SBS) redox system, or ceric ammonium nitrate (CAN) as initiators and finally by partial hydrolysis of the copolymerized product. Based on these experimental results, a preliminary techno-economic study for production of 3600 ton/year of the super-absorbent hydrogel was conducted. The economic study covered the process design for the two production lines via characterization of the principal equipment and related utilities through detailed material and energy balances all over the processes steps. The total fixed capital costs of hydrogel super-absorbent based on APS/SBS and CAN in powder and gel past forms were estimated taking into consideration the production of diammonium phosphate fertilizer as a by-product. The estimated costs for production of powder and gel paste hydrogel forms, using APS/SBS redox system, were 25,000L.E/ton and5,000 L.E/ton respectively, while those using CAN initiator were29,000 L.E/ton and 24,000 LE/ton respectively. Further, the profitability, the return of investment and the pay-out time for the production were assessed.

Keywords: super-absorbent polymer, hydrogel production, graft polymerization, cost estimation.

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INTRODUCTION

Sandy soils are characterized by low water-holding capacity and excessive drainage of rain and irrigation water below the root zone, leading to poor water and fertilizer use efficiency by crops. The problem of inefficient use of rain and irrigation water by crops is of great importance in semi-arid and arid region, where shortage of water is frequently experienced and water is often the limiting factor determining the size of cultivated area. Also, seed germination and plant development area are critically restricted because of low soil moisture content. The growth of plant and their quality are mainly a function of the quantity of fertilizer and water. For that, it is very important to improve the utilization of water resources and fertilizer nutrients. A possible means by which water loss due to drainage within sandy soils could be prevented is to mix the soil with hydrophilic polymer that is capable of swelling and retaining water up to 500 times its own weight[1,2]. Super-absorbent polymers have a typical three-dimensional network structure with a suitable degree of cross-linking. Not only is it able to absorb a huge amount of water to form a stable hydrogel, but also the absorbed water is hard to release under some pressure. The absorption behavior of super-absorbent polymer is related to their chemical structure, chemical saponification, the absorbing environmental and the nature of the solution. Recently, research on the use of super-absorbent polymers as water-managing tools for the renewable of arid and desert environment have attracted great attention [3-15]. Egypt's water requirement is increasing with time due to increase in number of population on one side and due to the government policy to reclaim new lands (desert lands) with development to redistribute the population growth concentration in the Nile Valley and Delta over a large area. In addition, water resources are limited to 55.5 billion m^3 from river Nile and ca 12 billion m^3 from underground water, which are barely enough to cultivate ca 8 million feddans.

Initiated by the above crucial issue, the present authors succeeded in producing an innovative hydrogel super-absorbent on pilot scale based on maize starch, which greatly proved its high efficiency in agricultural purposes in sandy soils, by field applications for different crops type, conducted at Researches and Production Station of National Research Centre (NRC), Al-Nubaria district, Al-Behaira Governorate[16].The pilot experiments were designed to produce the hydrogel in two forms :powder and gel past, based on two separate procedures by using ammonium persulphate and sodium bisulphite redox system andceric ammonium nitrate respectively as initiators. The objective of the present article is to carry-out a preliminary techno-economic study for the innovative super-absorbent hydrogel production line-in powder and gel-past forms-investigating its feasibility to support and guide decision-makers in their assessment for this locally manufactured strategic product.

PROCESS DESCRIPTION

Two target innovative hydrogel super-absorbents were produced in pilot scale level through the following three main steps:

i- Preparation of starch phosphate (St-P), by the use of a phosphate solution composed of a predetermined mixture of dihydrogen sodium phosphate and disodium hydrogen phosphate sprayed over a known amount of maize starch, in a batch reactor equipped with condensers.

ii-Polymerization of acrylonitrile (AN) onto St-P (St-P-PAN), with two different methods: firstly, by the use of redox system -composed of ammonium persulphate and sodium bisulphite aqueous solutions (APS/SBS)- for the first target hydrogel and secondly, by the use of ceric ammonium nitrate (CAN) for the second target hydrogel as initiators.

iii-Partial hydrolysis of the copolymerized product (S-St-P-PAN), by the addition of a predetermined amount of 48% sodium hydroxide solution with continuous mixing, precipitation of grainy solid product particles, followed by drying and grinding of the agglomerated particles to 1mm particle size. During the hydrolysis, ammonia gas is evolved and subsequently absorbed into 30% aqueous phosphoric acid solution to produce a by-product fertilizer, namely diammonium phosphate.

The two processes were fully described and reported earlier by the authors[16]. Two qualitative block diagrams demonstrating the hydrogel production by using APS/SBS and CAN initiators are illustrated in Figures (1, 2)respectively.

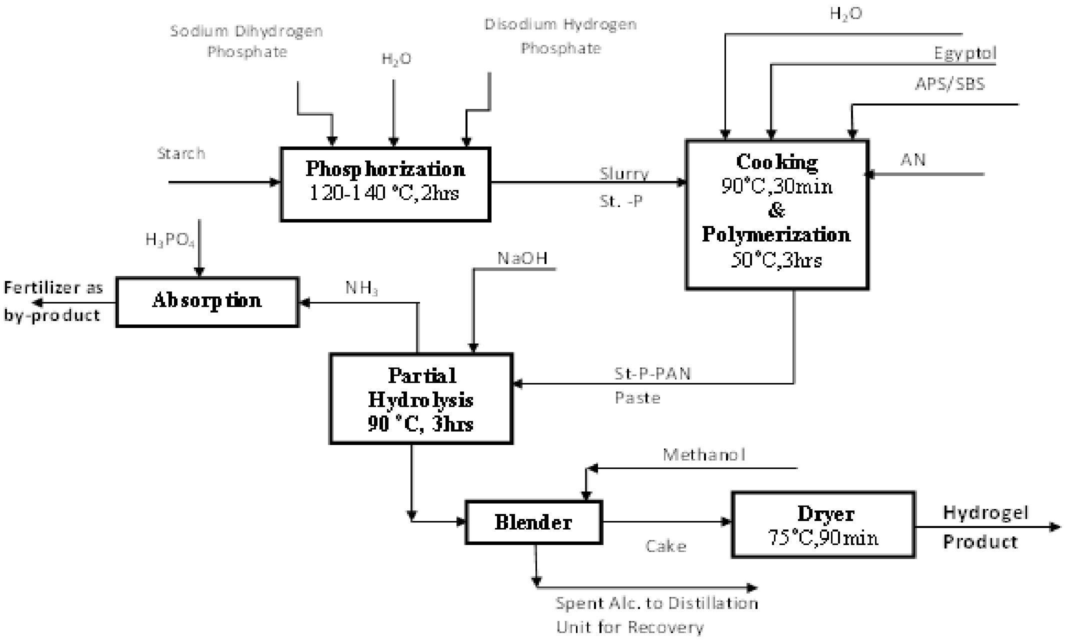

Figure (1): Block Flow Diagram for Hydrogel Production by using APS/SBS

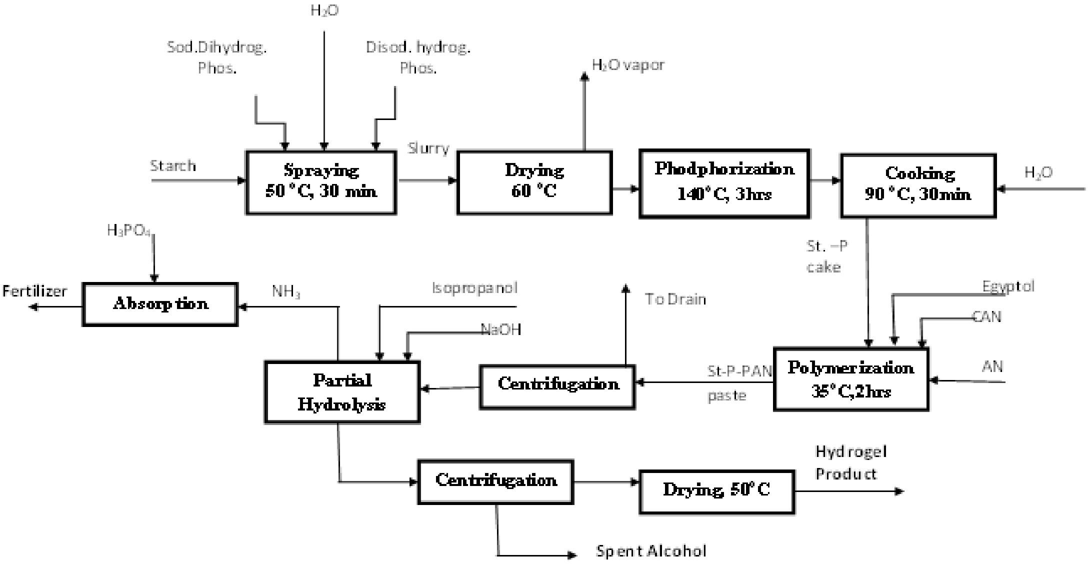

Figure (2): Block Flow Diagram for Hydrogel Production by using CAN initiator.

PROCESS DESIGN

Mass balance

According to data obtained from the pilot plant experiments[16], material balance calculations based on 1kg maize starch was scaled-up to 3600 ton/year hydrogel production within 300 days operating time through 3 working shifts/day (8 hours/ shift) and based on the following data for each technique، is presented in Figures (3,4):

Initiator Type	Operating batches	Production rate	Product solid content
APS/SBS	6 batches/day	2ton/batch	1.8 ton solid/batch
CAN	4 batches/day	3ton/batch	2.7 ton solid/batch

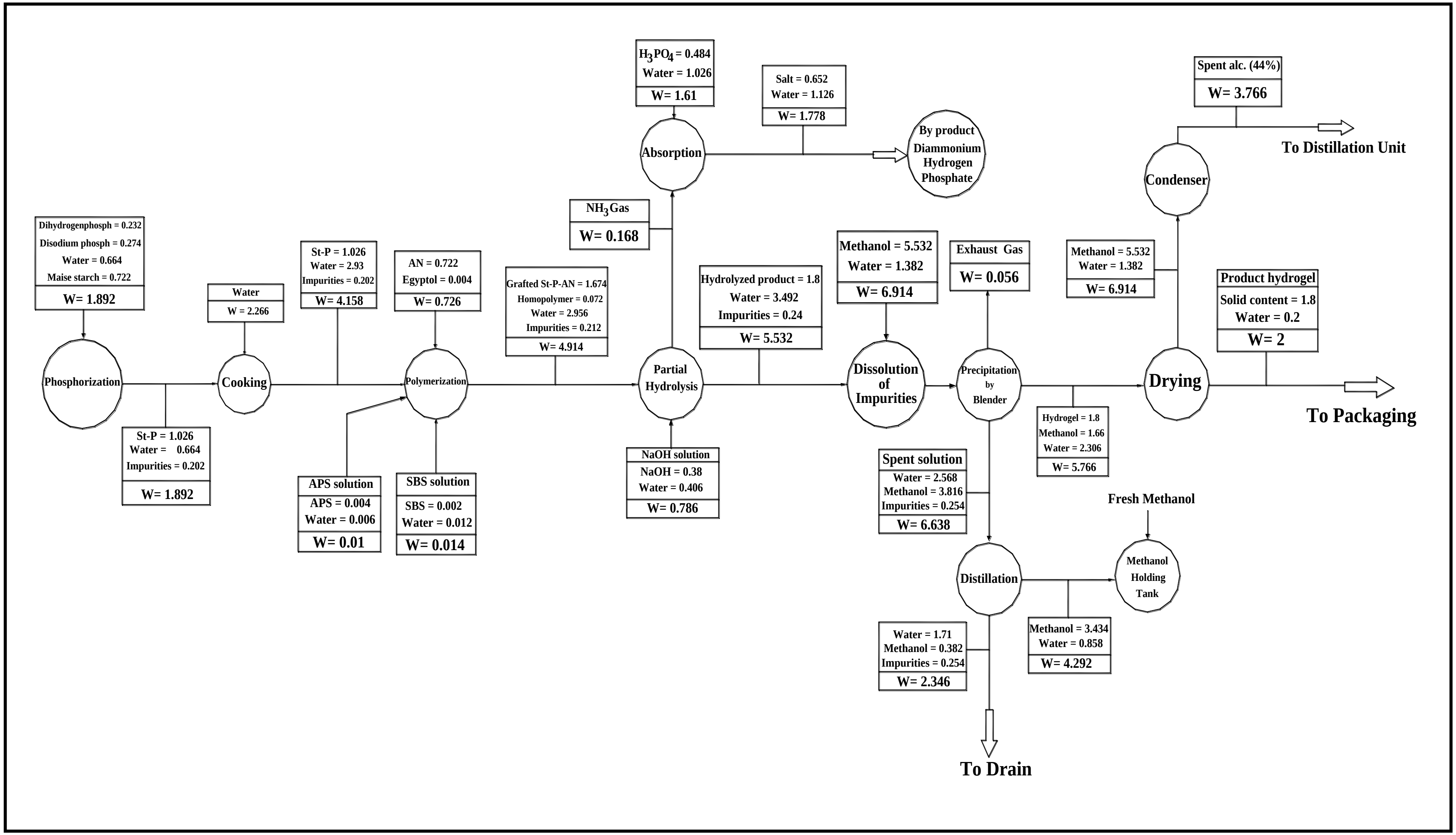

Figure (3): Mass balance flow diagram for 2 ton/batch hydrogel production using APS/SBS initiator.

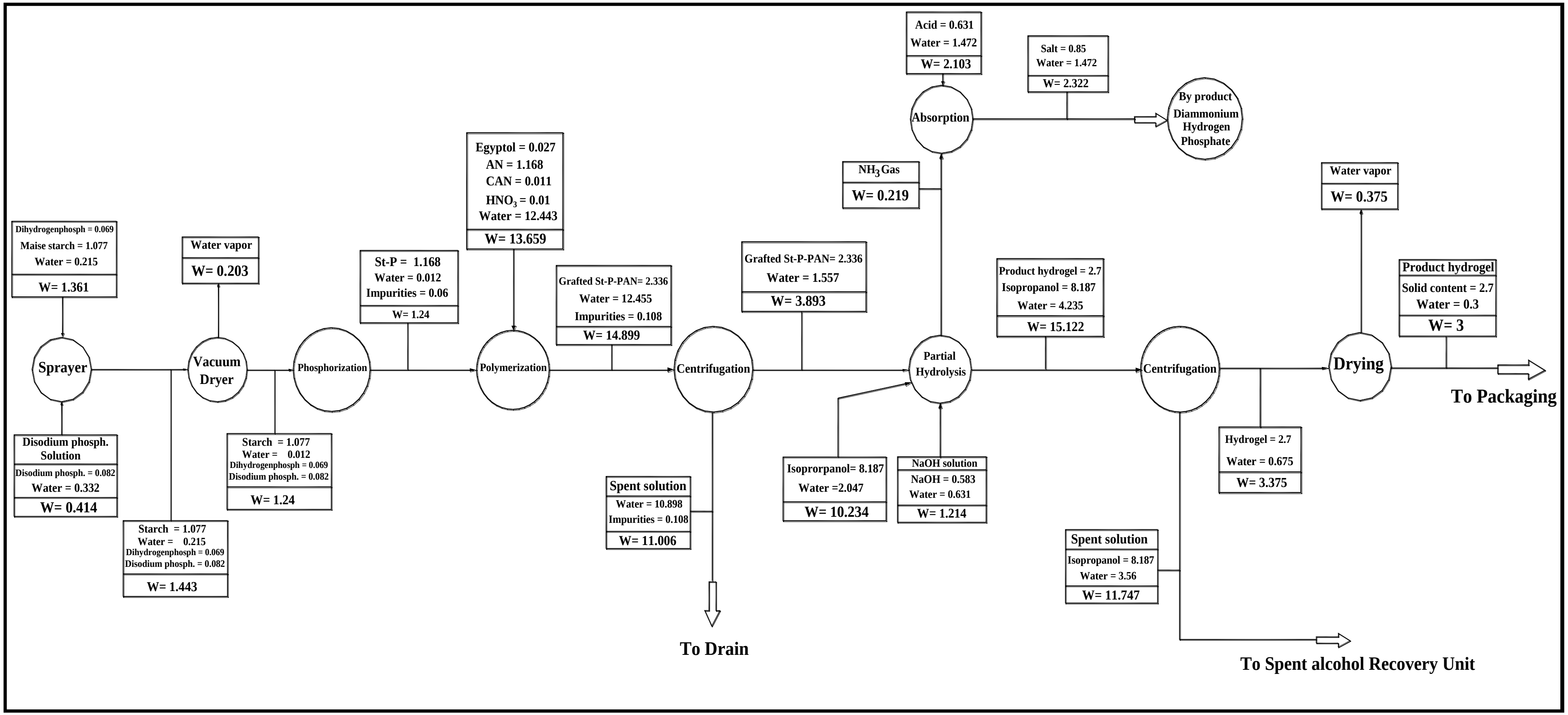

Figure (4): Mass balance flow diagram for 3ton/batch hydrogel production using CAN

Equipment sizing and selection[17]

The processes are essentially batch even though the drying step is continuous with respect to the APS/SBS initiator technique. For economic considerations, the two processes are planned and developed as to operate according to a proposed time schedule relevant to individual stepwise residence time, as illustrated in Figures (5,6), 3 hrs. and 5 hrs. interval each batch for APS/SBS and CAN initiator process respectively. The phosphorization reactor is designed to feed two reactors for polymerization alternatively. Coded equipment flow sheets [Sheets (7,8)] were prepared to obtain a systematic organization of sizing calculations. Energy balances and basis of design for some specific equipment are reported elsewhere [16].

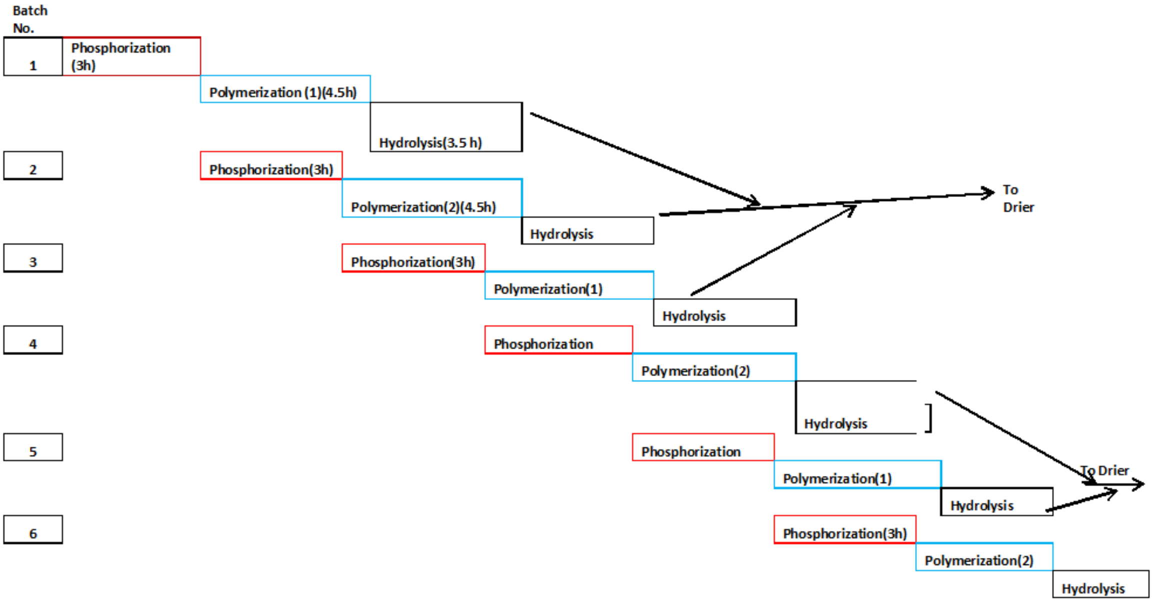

Figure (5): Sequential operation scheme for hydrogel production by APS/SBS initiators system.

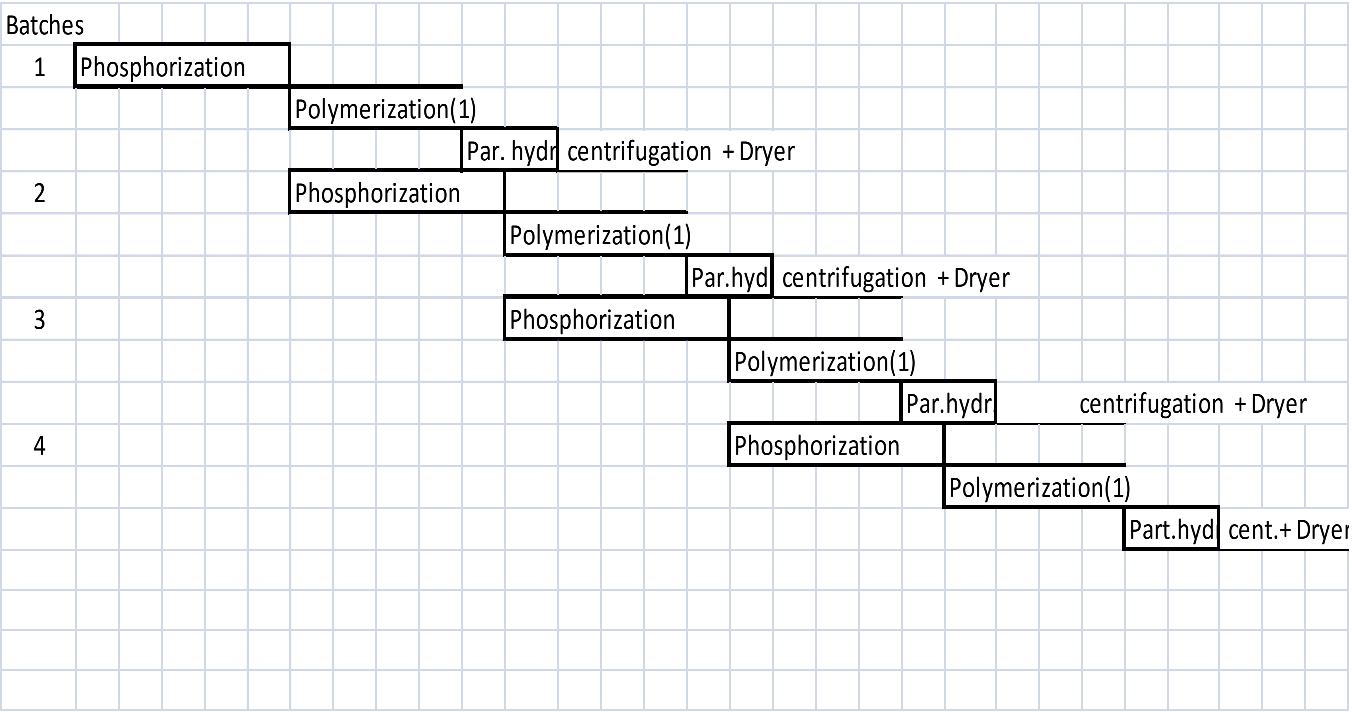

Figure (6): Sequential operation scheme for Hydrogel production using CAN as initiator.

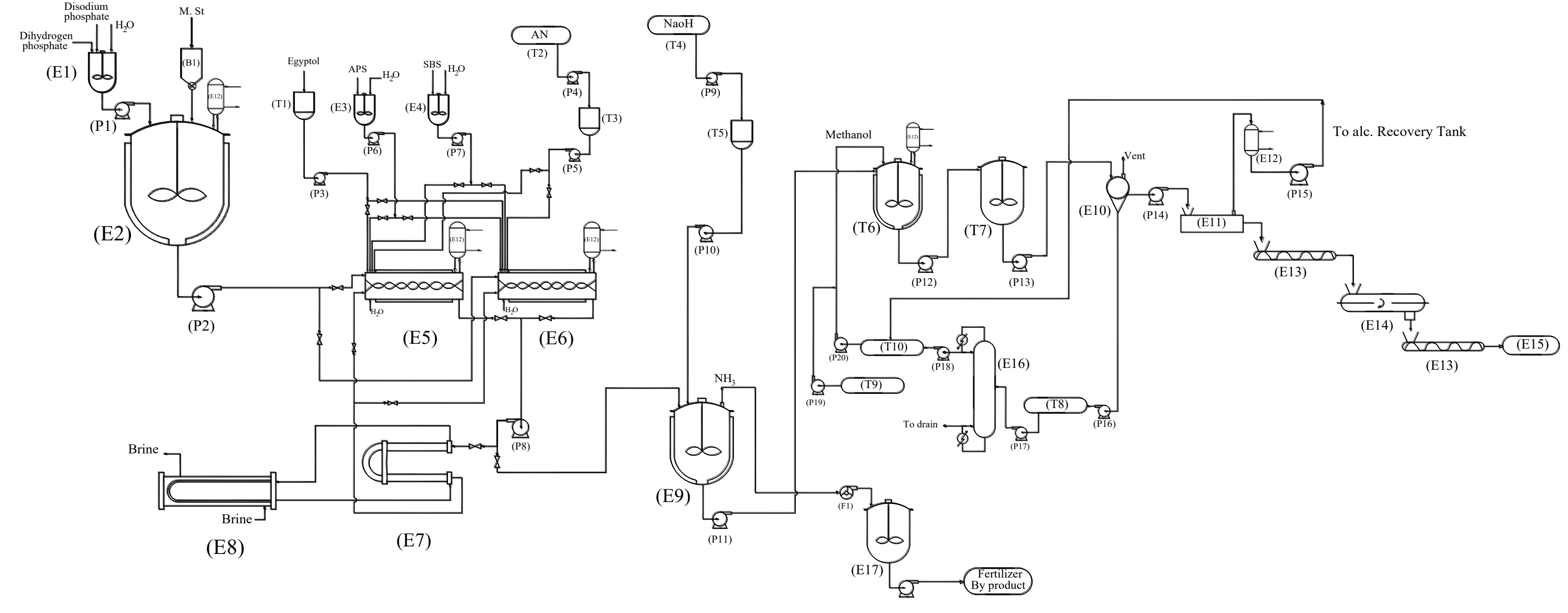

Figure (7): Equipment flow diagram for 2 ton/batch hydrogel production using APS/SBS initiator (12 ton/day).

Item	Description	Item	Description	Item	Description	Item	Description	Item	Description	Item	Description	Item	Description
E1	Sodium phospate dissolver	T3	Acrylonitrile feed tank	P8	Grafted product pump	P11	Hydrolyzed product discharge pump	E12	Condenser	E16	Methanol recovery unit	B1	Storage bin
P1	Phosphate solution Pump	P5	Acrylonitrile feeding pump	E7	Double-pipe exchanger	T6	Disperser/ Dissolution tank	P15	Condensate discharge pump	P18	Distillate discharge pump		
E2	Phosphorization Reactor	E3	Ammonium persulphate dissolver	E8	Chiller	P12	Dispersed product solution pump	E13	Screw Conveyor	T9	Fresh methanol storage tank		
P2	Starch phosphate Pump	P6	Ammonium persulphate feeding pump	T4	Sodium hydroxide solution storage tank	T7	Dispersed hydrogel product holding tank	E14	Hammer Mill	P19	Fresh methanol feed pump		
T1	Egyptol emulsifier feed tank	E4	Sodium bisulphite dissolver	P9	Sodium hydroxide solution charging pump	P13	Filter centrifuge feed pump	E15	Packaging machine	T10	Methanol recovery storage tank		
P3	Egyptol feeding Pump	P7	Sodium bisulphite feeding pump	T5	Sodium hydroxide solution feeding tank	E10	Filter centrifuge separator	P16	Spent methanol discharge pump	P20	Methanol feed pump		
T2	Acrylonitrile storage tank	E5	Polymerization Reactor (1)	P10	Sodium hydroxide solution feeding pump	P14	Dryer feed pump	T8	Spent methanol storage tank	F1	Fan		
P4	Acrylonitrile charging pump	E6	Polymerization Reactor (2)	E9	Partial hydrolysis Reactor	E11	Tunnel dryer	P17	Spent methanol feed pump	E17	Absorption reactor		

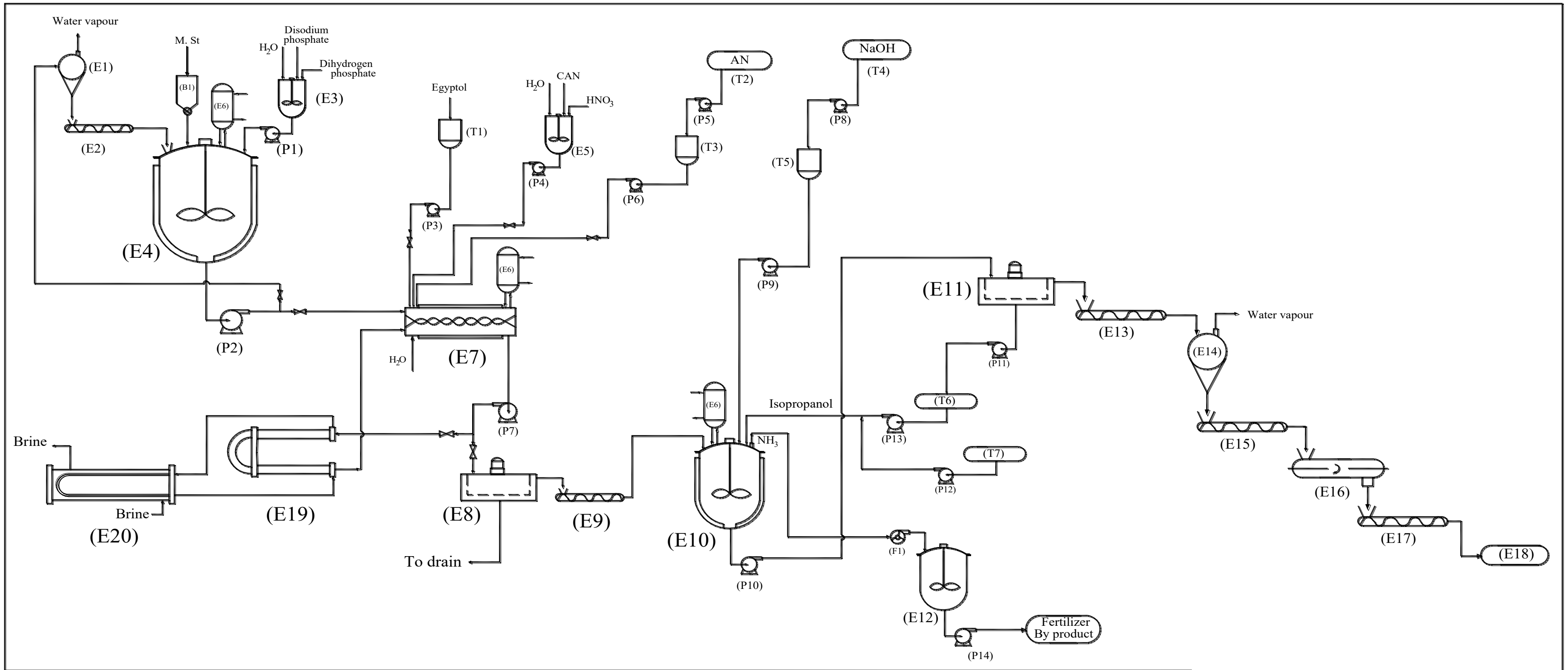

Figure (8): Equipment flow diagram for 3 ton/batch hydrogel production using CAN initiator (12 ton/day).

Item	Description	Item	Description	Item	Description	Item	Description	Item	Description	Item	Description
E1	Rotary vacuum dryer	E5	Ceric ammonium nitrate dissolver	P7	Grafted product pump	P10	Hydrolyzed product discharge pump	E12	Absorption reactor	B1	Storage bin
E2	Screw Conveyor	P4	Ceric ammonium nitrate feed pump	E8	Basket centrifuge	E11	Basket centrifuge	P14	Fertilizer by product discharge pump	E19	Double-pipe exchanger
E3	Sodium phospate dissolver	T2	Acrylonitrile storage tank	E9	Screw Conveyor	P11	Spent isopropanol discharge pump	E13	Screw Conveyor	E20	Chiller
P1	Phosphate solution Pump	P5	Acrylonitrile charging pump	T4	Sodium hydroxide solution storage tank	T6	Spent isopropanol storage tank	E14	Rotary vacuum dryer		
E4	Phosphorization Reactor	T3	Acrylonitrile feed tank	P8	Sodium hydroxide solution charging pump	T7	Fresh isopropanol storage tank	E15	Screw Conveyor		
P2	Starch phosphate Pump	P6	Acrylonitrile feeding pump	T5	Sodium hydroxide solution feeding tank	P12	Fresh isopropanol feed pump	E16	Hammer Mill		
T1	Egyptol emulsifier feed tank	E6	Condenser	P9	Sodium hydroxide solution feeding pump	P13	Isopropanol feed pump	E17	Screw Conveyor		
P3	Egyptol feeding Pump	E7	Polymerization Reactor	E10	Partial hydrolysis Reactor	F1	Fan	E18	Packaging machine		

Economic Evaluation for Hydrogel Production

Fixed- capital and Annual operating Costs

Cost estimation for the innovative proposed hydrogel production plant is required for preliminary evaluation of the designed schemes. In the following sections, unit production cost is estimated for two proposed options where the hydrogel is produced in powder form (option I) and in gel-paste form (option II), i.e., at the end of the partial hydrolysis reaction, the product –as gel- is packed in containers and is ready for use as such. For the sake of profitability analysis, the product cost of both hydrogel and the by –product phosphate fertilizer are estimated separately.

Table (1): Estimation of Fixed Capital Investments for Hydrogel Production Lines

Components	Powder Form, Cost in 1000LE		Gel Form, Cost in 1000LE	
	APS/SBS Process	CAN Process	APS/SBS Process	CAN Process
Direct Cost:				
1- Purchased equipment cost (E).	**5,756**	**4,242**	**2839**	**3,992**
2- Purchased equipment installation (32% E).	1,842	1,357	909	1,277
3- Instrumentation & control (20% E).	1,151	848	568	798
4- Piping (32 %E).	1,842	1,357	909	1,277
5-Electrical equipment & materials (10% E).	576	424	284	399
6- Buildings (including services) (20% E).	1,151	848	568	798
7- Services facilities and Yard improvement (40% E).	2,302	1,273	1136	1,198
8- Land (6% E).	345	255	170	240
Total direct cost (D)	**14,965**	**10,604**	**7,383**	**9,979**
Indirect Cost:				
1- Engineering & Supervision (5% D).	748	530	369	499
2-Construction expenses and Contractor's fee (7% D).	1047	530	517	698
3- Contingency (10% F.C.I.)	1,862	1,296	919	1,242
Fixed Capital Investment (F.C.I.)	**18,622**	**12,960**	**9,188**	**12,418**
Working Capital (15% T.C.I.)	**3,286**	**2,287**	**1,621**	**2,191**
Total Capital Investment (T.C.I.)	**21,908**	**15,247**	**10,809**	**14,609**

Total fixed direct and indirect costs- incurred during plant construction- represent the capital necessary for the installed process equipment with all auxiliaries that are needed for complete process operation. This estimation requires determination of the purchased- equipment cost. The other items, included in the fixed-capital cost are then estimated as percentages of the purchased –equipment costs[18].Costs of equipment locally purchased are estimated according to current costs as provided by local market, while imported equipment are estimated according to international firm suppliers included freight and customs charges (1$ = 7.8 L.E. based on year 2015). Values of the various percentages used in estimating the fixed-capital investment (F.C.I.) are demonstrated in Table (1).

The various cost elements, directly connected with the manufacturing operation are presented in Table (2). The prices of raw materials and utilities are obtained from reliable sources: - *Raw materials (commercial grade):*maize starch (4000 LE/ton), di-hydrogen sodium phosphate (5000 LE/ton), di-sodium hydrogen phosphate (5000 LE/ton), egyptol (25 LE/kg), acrylonitrile (12 LE/kg), ammonium persulphate (28LE/kg), sodium bisulphite (6 LE/kg), 48% aqueous sodium hydroxide (2000 LE/ton), methanol (5000LE/ton) and 30% aqueous phosphoric acid (7000LE/ton).

-*Utilities:* electricity (0.40LE/kW), steam (50 LE/ton), process water (3 LE/m^3) and cooling water (1.00 LE/m^3).

Table (2): Estimation of Annual Operating Costs for Hydrogel Production Lines

Components	Powder Form, Cost in 1000LE		Gel-paste Form, Cost in 1000LE	
	APS/SBS Process	CAN Process	APS/SBS Process	CAN Process
1-Total raw materials costs	82,306	102,232	49,816	93,946
2- Utilities	3,087	437	1,571	401
3-Maintenance (3% for buildings including concrete storage tanks and 5% for other installed equipment)	307	225	159	180
4-Operating labor *	900	750	500	675
5- Laboratory charges(10% of operating labor)	90	75	50	68
6-Administrative expenses (20% of operating labor)	180	150	100	135
Total Annual Operating Cost	**86,216**	**103,869**	**52,196**	**95,405**

*Operating labor is estimated based on the following terms:- using APS/SBS initiator, 4 main process steps for powder product line (36000 man-hrs /year) and 3 main process steps for gel-paste product line (20000 man-hrs /year)- using CAN initiator, 3 main process steps for powder and gel-paste product lines [(30000 man-hrs /year) and (27000 man-hrs /year) respectively]- 5000 LE/ month average salary per labor and 200 man-hr/month i.e. 25 LE/ man-hr**.**

Unit Production cost

The production cost is the sum of total annual operating cost and total depreciation rate per unit product capacity. Annual depreciation rate is estimated based on a useful-life period of 10 years of the fixed capital cost excluding buildings and concrete equipment, while buildings and concrete equipment are depreciated based on 30 years lifetime. Recalling that the designed productivity for hydrogel product in powder form is 3600ton/year while, according to the mass balance, the annual productivity of hydrogel gel-paste products is 9958 ton/year and4050 ton/year using APS/SBS and CAN initiators respectively, the unit production cost for each hydrogel product is illustrated in Table (3).

Table (3): Estimated Hydrogel Products Costs

Item	Powder product		Gel-state product	
	APS/SBS	CAN	APS/SBS	CAN
Depreciation Rate, LE/year	1,733,467	1,230,267	881,933	1,176,067
Product Cost, LE/kg	25	29	5	24

Cost Estimation of the diammonium hydrogen phosphate (by-product fertilizer).

Table (4): Estimation of Fixed Capital Investment for fertilizer production

Components	APS/SBS initiator	CAN initiator
	Cost, in 1000 LE	Cost, in 1000 LE
Direct Cost		
1- Purchased equipment cost (E).	50	77
2- Purchased equipment installation (20% E).	10	15.4
3- Instrumentation & control (5% E).	2.5	3.85
4- Piping (20 %E).	10	15.4
5-Electrical equipment & materials (10% E).	5	8
6- Buildings (including services) (20% E).	---	---
7- Services facilities and Yard improvement (40% E).	---	---
8- Land (6% E).	---	---
Total direct cost (D)	**77.5**	**119.65**
Indirect Cost		
1- Engineering & Supervision (3% D).	2.325	3.59
2-Construction expenses and Contractor's fee (5% D).	3.875	5.98
3- Contingency (10% F.C.I.)	9.3	14.36
Total indirect cost	**15.5**	**23.93**
Fixed-capital investment (F.C.I.)	**93**	**143.58**

Table (5): Annual operating costs for fertilizer production

Component	APS/SBS initiator	CAN initiator
	Cost, in 1000 LE	Cost, in 1000 LE
1-Total raw materials costs*	14,490	12,617
2-Utilities: Electricity	3	2
3-Maintenance (5% for installed equipment)	2	4
4-Operating labor	----	----
5- Laboratory charges(10% of operating labor)	----	----
6-Administrative expenses(20% of operating labor)	----	----
Total Annual Operating Cost	**14,495**	**12,623**

*Cost of 30% H_3PO_4 = 5000 LE/ton, the ammonia gas cost is considered nil.

Table (6): Diammonium hydrogen phosphate production cost (37% conc.)

Initiator	Annual production, ton/year	Annual operating cost,LE/year	Annual depreciation rate, LE/year	Fertilizer unit product cost, LE/kg
APS/SBS	3200	14,495000	9,300	**4.5**
CAN	3060	12,623,000	14,358	**4**

As mentioned above, the equipment cost relevant to the ammonia absorption into 30% aqueous phosphoric acid-to produce about 37% diammonium hydrogen phosphate fertilizer as by-product-is excluded from the above cost evaluation. Tables (4-6)depict the fixed-capital investment and the annual operating cost in order to estimate the fertilizer solution product cost obtained with both initiators used.

Profitability analysis

In general, the profitability is related to the income and expenses of a productive facility, so that a sound judgement can be taken when an investment is to be made. In other words, this analysis is the final decision as to whether a given project should be supported or not. One of the most commonly used methods for profitability evaluation is the determination of the rate of return on investment via the following expression:

$$\% \text{ Return on Investment (R)} = [\text{Profit} / \text{T.C.I.}] \times 100$$

Table (7) demonstrates the cost and profit summary for hydrogel production in its two produced forms ,by using either initiator, as principal product and its fertilizer by-product solution. Sales price are estimated in view of market competition as follows:

- Hydrogel in powder form = 30 LE/kg (for APS/SBS method); 35 LE/kg (for CAN method).
- Hydrogel in gel paste form = 10 LE/kg (for APS/SBS method); 29LE/kg (for CAN method).
- 37% aqueous diammonium hydrogen phosphate = 6.5 LE/kg

Table (7): Profit summary for hydrogel proposed plant using both initiators

Item	APS/SBS		CAN	
	Powder form	Gel Paste form	Powder form	Gel Paste form
Total products cost, LE/year	104,400,000	64,200,000	116,640,000	109,440,000
Total products value, LE/year	125,600,000	77,360,000	142,830,000	134,280,000
Gross profit, LE/year	21,200,000	13,160,000	26,190,000	24,840,000
Net profit*, LE/year	10,176,000	6,317,000	12,571,000	11,923,000
T.C.I., LE	22,018,000	10,915,000	15, 416,000	14,778,000
% R	**46**	**58**	**80**	**80**
Pay-out time, year	**2.16**	**1.73**	**1.23**	**1.25**

*Income tax rate = 52%

CONCLUSIONS

The production of innovative super-absorbent hydrogel, the target product, with different shapes and types and having superior water holding capacity in agriculture field practices, is thoroughly investigated economically. Two different technologies have been studied regarding the initiator type in the graft-polymerization step for the hydrogel production. The first method was by using available, locally manufacturing, environmentally friendly and low cost ammonium persulphate / sodium bisulfite redox system. The second method was by using ceric ammonium nitrate as initiator, which, although it yields good results, yet, its availability is less and its cost is relatively higher. Finally, although using the ceric ammonium nitrate shows better profitability (around 2% increase), yet the use of the first method in the super water absorbent hydrogel production is recommended in view of the above properties.

ACKNOWLEDGMENT

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