

Evaluation of struvite precipitated from chemical fertilizer industrial effluents

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ABSTRACT

The process of struvite precipitation and removal of $\text{NH}_4^+\text{-N}$ from industrial waste streams were studied by laboratory experimental work. Struvite, the slow release fertilizer was prepared by addition of magnesium and phosphate sources with calculated stoichiometric ratio to optimize reagent dosage and makes the precipitation more efficient. Liquid bittern (LB) was added as low cost magnesium source, containing 73% magnesium. Three industrial effluents from the fertilizer factory, proved to be cost –effective for struvite production. The ammonia removal ratio was 80% from the nitric acid stream, 57% from the ammonium nitrate stream, and 54.2% from the ammonium sulfate stream. The yield of struvite was 1.15 g/L, 1 g/L, 0.79 g/L and 0.5 g/L recovered from ammonium sulfate stream, nitric acid stream, ammonium nitrate stream and mixed stream respectively. Struvite formation was later verified by analyzing the morphology and composition employing scanning electron microscope (SEM) and X-ray Diffraction (XRD), respectively. A preliminary techno – economic evaluation for struvite production predicted from both pilot scale and industrial scale was studied and supported recovered struvite for potential use as a renewable fertilizer.

Key words: slow release fertilizer, nutrients recovery, industrial effluent, liquid bittern, struvite.

INTRODUCTION

Struvite precipitation is one the innovative physico-chemical processes which can majorly contribute for the removal of $\text{NH}_4^+\text{-N}$ or phosphorous forming complex under required conditions. It is also an ecologically sound technology which is not only cost –effective, but also sustainable in terms of possible recovery of recyclable constituents from industrial effluent rich in nutrients.

$\text{NH}_4^+\text{-N}$ has been identified as one of the major toxicants to microorganisms in the treatment system, suggesting that pretreatment prior to the biological treatment system is required to reduce the concentration of $\text{NH}_4^+\text{-N}$ [1]. Nitrogen contamination is highly toxic and it would adversely affect aquatic life if it is discharged above sustainable limit causes the death of fish [2]. The high content of ammonia nitrogen is the major factor that affects the toxicity of wastewater. Majorly fertilizer and dye manufacturing industries have high $\text{NH}_4^+\text{-N}$ content in their effluent [3]. Therefore the treatment of effluent for removal, recovery / recycle for ammonia nitrogen is essential.

Some industrial effluents are both characterized by relatively high concentrations of phosphorous and nitrogen (especially ammonia). The wastewater produced from dairy industry in cheese whey arise environmental pollution if there is no recycling unit. Semiconductor wastewater generally contains high levels of ammonia ($\text{NH}_4^+\text{-N}$) and phosphate (PO_4) [4].

Around the world there is an augmentation on production of fertilizers containing phosphate with increasing demand for phosphate rock by 1.5% each year [5]. About 85% of the phosphate is used for production of fertilizer and there are 7 -billion tons of phosphate rocks as P_2O_5 remaining in reserves. Considering 40 million tons of P as P_2O_5 consumption each year, the available resources of P are expected to be exhausted in 100/250 years [6]. Japan use of Fertilizer is 321 Kg/hectar, France 240 Kg/hectar, England 283 Kg/hectar, Greece 115 Kg/hectar, Spain

155Kg/hectar and the world average of fertilizer usage is 116 Kg/hectar. As soil lacks nitrogen and phosphorous the fertilizer usage is necessary in agricultural growth.

Therefore, finding a cheap method to recover such materials from waste streams can provide a break through solution. One of the recent innovations is production and recovery of struvite ($\text{Mg} \cdot \text{NH}_4 \text{PO}_4 \cdot 6\text{H}_2\text{O}$) from the waste. If the formation of struvite is controlled, then it can be beneficiary since its precipitation removes $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ from the water and the precipitate has the potential use as a fertilizer [7].

Struvite (MAP) magnesium ammonium phosphate, yield one of the most nutritive fertilizers because it consists of Mg, N and P as micro and macro nutrients for soil fertilities, in addition it is a concentrated, granular, non-sludgy, non-odorous, and slow-release fertilizer and fairly valuable by-product. Struvite can be effectively used as a slow-release fertilizer at high application rate without a risk of damaging plants. Suggested uses are diverse and include ornamental plants, young trees in forest, grass, orchards and potted plants. If high recovery efficiency can be achieved in wastewater treatment plants, then recovered products can be used as a substitute of existing fertilizer products. There are also fertilizer companies using struvite as an additive and they mix it with other inorganic and organic materials to adjust the amount of nitrogen, phosphoric acid and potassium.

Struvite or MAP as shown in Fig (1) is a white crystalline solid substance consisting of magnesium, ammonium, and phosphorus in equal molar concentrations.

In wastewater containing both soluble $\text{PO}_4^{3-}\text{-P}$ and $\text{NH}_4^+\text{-N}$, struvite crystallizes if Mg^{2+} and alkali are added [8].

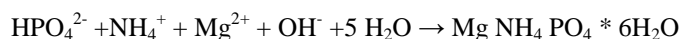


Fig. (1) Struvite picture in powder and granulated forms

MAP complex process is pH sensitive method. A complex becomes insoluble at pH above 8.5 and hence accurate control of pH has to be shown in precipitation operating conditions. Doses of Mg and P depend on the stoichiometric calculations. The recovered struvite contains hardly any toxic substance, and can be sold to fertilizer companies as a fertilizer raw material [9]. The formation of struvite crystals is a method which converts the hazardous waste into non-hazardous useful nutritious resource [10]. MAP process can stand tall for green revolution [11].

In this study five different effluents of fertilizer-company will be used to recover ammonia depleted (during nitrogen fertilizer production) as struvite.

MATERIALS AND METHODS

Five grape samples have been taken from Chemical fertilizer industry's streams. Ammonium Nitrate stream, Ammonium Sulfate stream, Nitric acid stream, Treatment unit stream and Mixed stream were used as test samples. The experiment is carried out in a beaker of capacity 3L with moderate agitation with speed (100 rpm.) for each experiment. NaOH solution (1N) is used to adjust effluent streams pH to the required value. All samples streams are nearly alkaline except the third stream sample which needed treatment with more NaOH as shown in Table [1] [12].

Table (1) Characteristics of waste effluents before Struvite precipitation

Effluent type	pH value	TDS mg/L	Cond. mS/cm	SO ₄ ²⁻ mg/L	NH ₄ ⁺ mg/L	PO ₄ ³⁻ mg/L	COD mg/L	Ca ⁺⁺ mg/L	Mg ⁺ mg/L
Ammonium Nitrate	9.27	23.6	4.72	108	0.033	45.77	96	0.32	0.115
Ammonium Sulphate	8.07	6.80	13.77	448	0.120	98.85	104.5	1.204	0.361
Nitric Acid	8.62	1.08	2.23	264	0.251	69.62	50.5	0.69	0.339
WW trmnt Unit*	2.02	7.42	14.90	816	0.11	76.15	30.5	----	----
Mixed effluents	9.26	4.89	9.78	888	0.106	23.85	33	0.42	0.988

*Trmnt = treatment

Effluent streams are subjected to full chemical analysis according to standard methods for examination of water and wastewater for (ammonia, phosphorous, magnesium, hardness, calcium, conductivity, pH value, dissolved solids and others). Calculated quantities of precipitating agents can be added. Liquid Bittern(LB) as low cost source of magnesium was used and their characteristics are shown in Table (2).

Table (2) Characteristics of liquid bitten used as source of magnesium

Element	Value(mg/L)
TDS	292
Calcium	1600
Magnesium	73.84
Sodium	21.76
Chlorides	218.63
Sulfate	3.2
Carbonate	0.5
Potassium	9.81
Bicarbonate	1.73
Bromine	12
Boron	70
Iodine	5
Lithium	0.31
Conductivity	583mS/cm

RESULTS AND DISCUSSION

After addition of the precipitating agents, pH of wastewater streams has to be maintained at about 9.5 for higher yield of struvite precipitation. When we compare the data analyzed in Table(1) and Table(3), we notice the sharp decrease in ammonia concentration mainly in streams of ammonium nitrate from 0.033 mg/L to 0.015 and in nitric acid stream from 0.25 to 0.05 which prove the efficient recovery percentage of more than 57.2% in ammonia nitrate stream and about 80% in nitric acid stream, with struvite yield of 0.79 and 1 g/l respectively. Struvite yield from ammonia sulphate was the highest of 1.1g/L as shown in Table (4).

Table (3) Analysis of waste Effluents after Struvite precipitation

Effluent type	pH value	TDS mg/L	Cond. mS/cm	SO ₄ mg/L	NH ₄ ⁺ mg/L	PO ₄ ³⁻ mg/L	COD mg/L	Ca ⁺⁺ mg/L	Mg ⁺ mg/L
Ammonium Nitrate	8.94	20.12	36.56	128	0.015	11.0	40.5	0.24	0.089
Ammonium Sulphate	9.13	6.39	12.47	260	0.055	11.0	34.2	0.54	0.403
Nitric Acid	8.01	2.03	4.10	477	0.050	8.77	42	H*	5.626
WW treatment Unit	8.90	6.64	12.95	532	0.131	6.92	8.50	0.554	0.273
Mixed effluents	9.21	5.21	10.04	616	0.107	4.154	19	0.28	0.110

*H= very high

The same for phosphorous reduction percentage which is performed with struvite precipitation technique at their optimum operating parameters of pH, precipitation time and agitator speed to give highest reduction percentage in ammonium sulphate streams of about 89% followed by nitric acid stream of 87.4% reduction in phosphorous content which was crystallized as struvite .

The sequential addition of required reagents should be, (LB) as magnesium source followed by phosphate and then allowing the mixture to agitate for about 30 to 60 minutes at moderate speed (100 rpm) and then record the results. After one hour of continuous stirring, precipitate is allowed to settle down the container over-night to allow product to agglomerate and give high crystal growth [13].

Table (4) illustrates the changes of ammonia, phosphate, sulfate and chemical oxygen demand in the five streams after struvite precipitation. The percentage of COD removal showed trends within range (16 – 58%)[14] and[15]. No significant increase in the pH was maintained after treatment. Residual phosphate was determined in some

streams. This phosphate may be formed at lower pH, further crystallization and precipitation of struvite was then inhibited, thus residual concentration of phosphate was maintained.

Table (4) Results of percentage reduction of ammonia, phosphate, sulfate and chemical oxygen demand

Effluent type	SO ₄ ²⁻ (%)	COD (%)	PO ₄ ³⁻ (%)	NH ₄ ⁺ -N (%)	Yield (g/L)
Ammonium Nitrate	---	58.33	76.08	57.5	0.7913
Ammonium Sulphate	41.96	67.3	88.87	54.2	1.1466
Nitric Acid	---	16	87.4	80.1	1.0003
Waste Water treatment Unit	---	---	---	--	---
Mixed effluents	30.63	42.4	82.58	--	0.5053

3.1. SEM and XRD Analysis precipitation of struvite from ammonium nitrate stream

To assess the quality of struvite created through precipitation, the four streams were analyzed by XRD and SEM analysis Fig (2) to Fig (5). The XRD pattern generated from these samples matched the database model for struvite.

Struvite is precipitated from ammonium nitrate stream in pure elongated needle crystal shape as shown in image (2). The needle-shaped crystals precipitated with regular size of radius 4.7nm -7.6 nm, and of length of 26.7 nm – 54.1 nm. The XRD of this struvite is shown in Fig(2) which illustrates the main five indicative peaks of struvite.

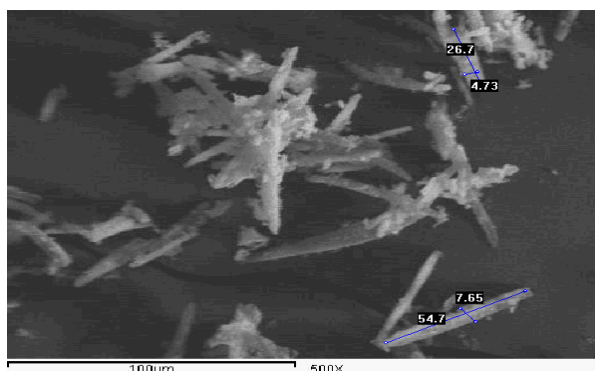


Image (2) SEM view of struvite crystals precipitated from Ammonium Nitrate stream

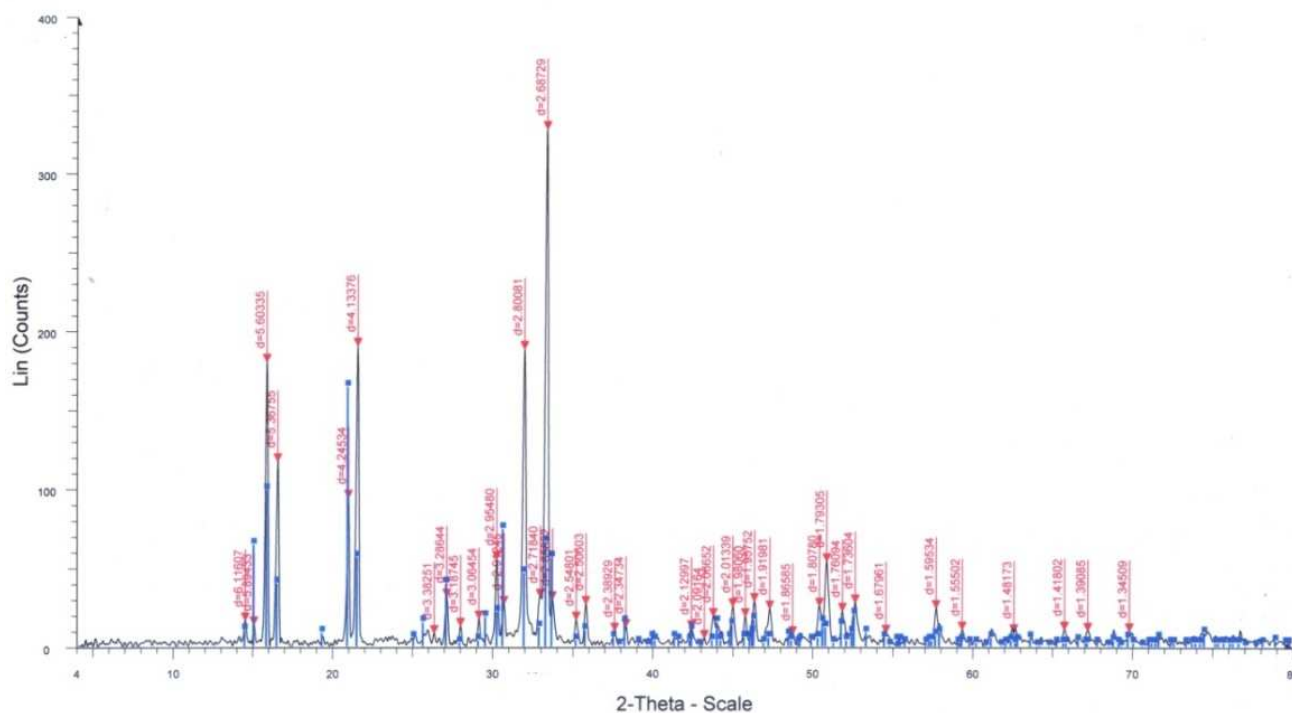


Fig (2) XRD of struvite precipitated from Ammonium Nitrate stream

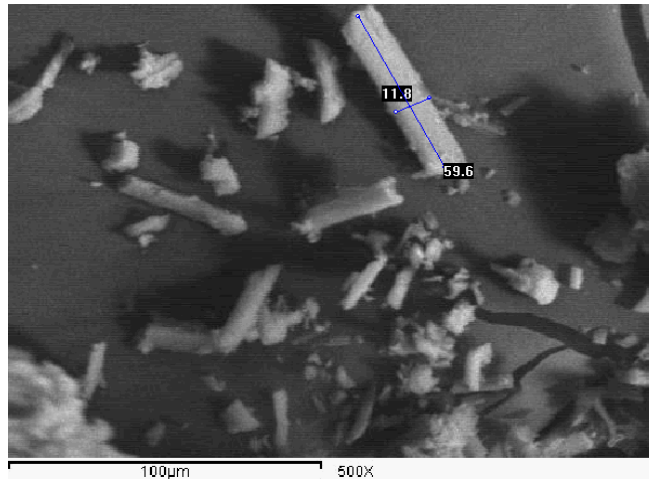


Image (4)ESM view of struvite crystals precipitated from Nitric Acid stream

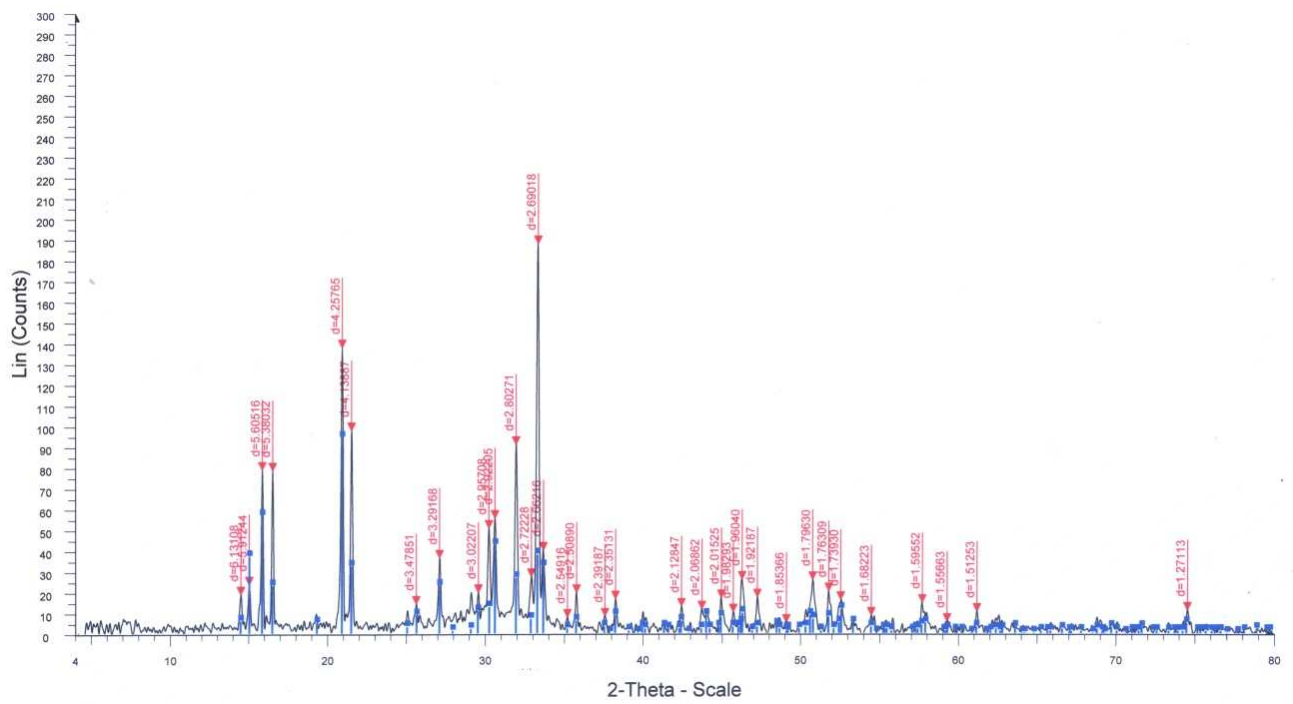


Fig (4) XRD of struvite precipitated from Nitric Acid stream

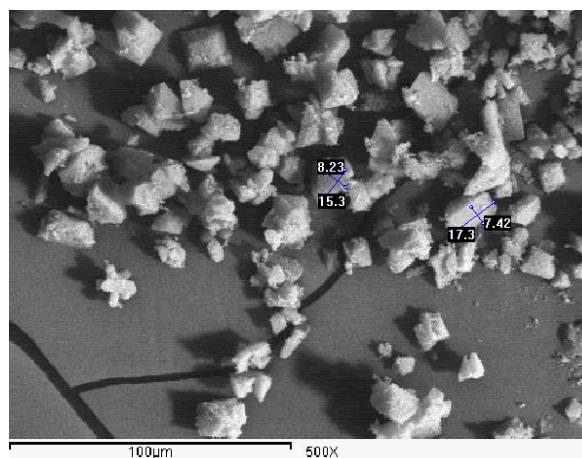


Image (5)ESM view of struvite crystals precipitated from Mixed stream

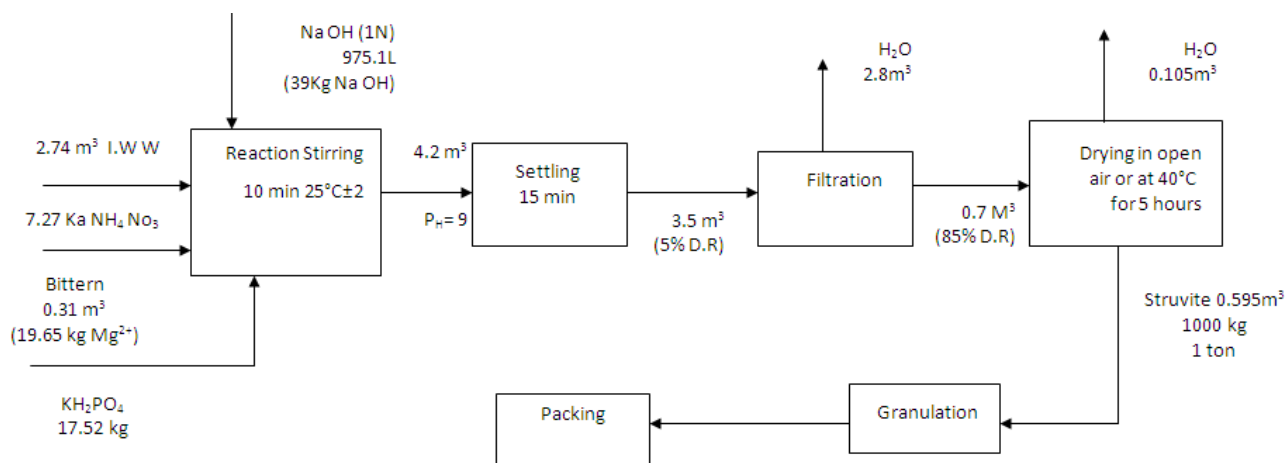


Fig (7) Block Flow Sheet for Struvite Production at Industrial Scale (1 ton/shift)

5.1. Total capital investment costs

Equipment sizes based on the mass production and cost estimation of the process equipment has been estimated as presented in Table(5) [16].

Table (5) Total Capital Investment (TCI)

Item	No Unit	Cost L.E
A. Direct Cost (DC)		
• Purchased Equipment (PE*)		
• Wastewater storage tank concrete lined 2m ³	1	5000
• Brine storage tank concrete lined 5m ³	1	7500
• Reactor, Reinforced concrete, Lined & 5m ³ capacity with Mechanical Stirrer	1	15000
• Settler, Reinforced concrete, Lined provided with bottom skimmer& 5m ³ capacity	1	8500
• Filer press (2.5m ³)	1	30000
• Drying beds (1m ³)	2	50000
• Granulator	1	10000
• Packing Unit (500 kg/hr)	1	6000
Total purchased Equipment		132000
• Purchased equipments installation (35% of P.E)		46200
• Instrumentation control (10% of P.E)		13200
• Piping (15% of P.E)		19800
• Electrical (10% of P.E)		13200
• Buildings (15% of P.E)		19800
• Yard Improvement (4% of P.E)		5280
• Land & Service Facilities (10% of P.E)		13200
Total Direct Cost		130680
		2626800
B. Indirect Cost – (IC) (15% of FCI)		
• Engineering & Supervisor (5% DC)		13134
• Contractor fee 's (2% of DC)		5254
• Contingency (6% of FCI)		17941
Total Indirect Cost (IC)		36329
C. Fixed Capital Investment (FCI)		
FCI = DC + IC		299009
D. Working Capital (10% of FCI)		
		29901
Total Capital Investment = DC +IC+WC		328910

*All equipments are locally made in Egypt.

5.2. Operating Cost

In addition to raw materials cost as estimated according to actual consumption from pilot experimental results and prevailing costs, other components of operating costs are presented in Table (6, 7, 8&9)

Table (6) Annual Raw Materials Cost

Name of Material	Price / Ton L.E	Annual amount 1 kg/y	Annual rat material cost L.E/year
• Sodium hydroxide	200	40	8
• Potassium di hydrogen phosphate	70500	35	2467.5
• Waste water (NH ₄ NO ₃)	500	150000	150000
• Bittern* (Mg) ⁺⁺			
Annual raw materials cost			152476

Table (7) Annual Direct Production Cost

Item	Cost L.E/year
• Annual raw materials cost	152476
• Operating labors (20% of TPC)	304951
• Direct supervision (0.05% of OL)	76238
• Utilities (0.2% of TPC)	304956
• Maintenance (10% of FCI)	29901
• Operating supplies (1% of FCI)	2990
• Laboratory charges (0.05% of OL)	60990
• Patents & Royalties (0.06% of TPC)	91486
Direct production cost	1023988

*Transportation cost of bittern considering no actual cost for waste bittern

Table (8) Fixed Charges Cost

Item	Cost L.E/year
• Depreciation (10% of FCI)	29901
• Local Taxes (4% of FCI)	11960
• Insurance (1% of FCI)	2990
Total fixed charges	44851
Plant overhead (10% of TPC)	152476

Manufacturing cost = Direct cost + Fixed charges + Plant overhead = 147252 L.E

Table (9) General Expenses

Item	Cost L.E/year
• Administration Cost (4% of TPC)	60990
• Distribution & Selling Cost (10% of TPC)	152476
• Research & Development (5% of TPC)	76238
• Financing (1% of FCI)	2990
Total General Expenses	292694

Total production cost = Manufacturing cost + General Expenses = 1514009 L.E / 600 tons

= 2523 L.E / ton = 2.5 L.E / kg = 31.25 NRs* / kg

The struvite market value is between 25 and 57 NRs/ kg with a best estimate of 41 NRs/kg [17]

Our struvite is Mg NH₄ PO₄ · 6H₂O

1.6 : 0.6 : 1.6 by mole, so nitrogen content in our struvite is 5.54%.

Produced struvite is considered as mixed fertilizer (15.4% Mg, 4.3% NH₄ and 35.6% PO₄) with production cost 2523 L.E/ton.

The calculation of the product cost as prices of each component in local market according to Table (10).

*1 Euro = 100 NRs = 8 L.E

1NR = 0.08 L.E

Table (10) Calculation of Struvite Price

Fertilizer	Effective element (%)	Cost of effective element (L.E /ton)
• Magnesite (MgSO ₄ .10 H ₂ O)	8% Mg	2000
• Ammonium Nitrate (NH ₄ .NO ₃)	22.5% NH ₄	1400
• Superphosphate Ca(H ₂ PO ₄) ₂ .H ₂ O	75.4% PO ₄	700

The estimated total price of the mixed fertilizer (struvite) produced will be calculated as the addition of each component as shown in Table (11).

Table (11) Estimation of produced struvite price

Component	%	price (L.E/ton)
Mg	15.4	3850
NH ₄	4.3	267.5
PO ₄	75.4	330.5
Total		4448 L.E/ ton Considered as selling price

So total selling price = 4000 x 600 = 2400000 L.E

Total production cost = 2523x 600 = 1514003 L.E

Profit = 2400000 - 1514003 = 885991 L.E

SRR % = $\frac{\text{Profit}}{\text{TCI}} \times 100 = \frac{885991}{328910} \times 100 = 269\%$

Payback Period = $\frac{\text{TCI}}{\text{Profit}} \times 12 = 4.45 \text{ months} = 5 \text{ months}$

CONCLUSION

In this study struvite was recovered from waste effluents of chemical fertilizer industry. The stoichiometric molar ratio of Mg²⁺: NH₄⁺-N: PO₄²⁻ was 1:1:1 which was sufficient for ammonia removal by 80% and produced yield of about 1g/L from the Nitric Acid effluent in the struvite precipitation. The crystal phase of struvite was obtained by XRD and morphologies were analyzed by SEM. The crystal morphologies indicated high purity in all single streams (ammonium nitrate, ammonium sulphate and Nitric acid), but the recovered crystals from the mixed stream showed contamination which slightly inhibited the rate of crystal growth. The preliminary economic study predicted, indicated significant mass production of struvite and proved that struvite technology is an economic efficient technique to avoid harmful effects of eutrofication with successful production of slow-release fertilizer rich in ammonia and phosphorous..

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REFERENCES.

- [1] Nigam P, Armour G., Banat I. M., Singh D, Marchant R., *Bio Tech* **2000**, 72, 219 – 226.
- [2] Lawrence K. Wang, Norman C. Pereira, Yung – Tse Hung, *Advanced Biological Treatment processes*. Wiley Inc. pub., edition 1, pp 345.
- [3] Paul N. Cheremis, *Waste minimization and cost reduction for the process industries in off (treatment of effluent fertilizer industry example)*, **2003**, edition 1, pp 285 – 299.
- [4] Hong – duck Ryu, Chae – Sung Lim, Sang – Ill Lee *Journal of Hazardous Materials*, **2012**, 227 – 228, 1-484.
- [5] Steem I, Phosphorous availability in the 21st Century Management of a Non – Renewable Resource. , **1998**. *Phosphorous and Potassium*, 217 – 25 -31.
- [6] Shu, L., Schneider, P., Jegateesay V., Jhoson, J., *Bioresource Technology*, **2006**, 97, 2211 – 2216.
- [7] Doyle D. and Parson A. *Water Research* **2002**, 36, 3925 – 3940.
- [8] Stowa, Web Site, WWW.Stowa-selectedtechnologies.nl, Retrieved on August 07, **2006**.

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- [9] Struvite role in phosphorous recovery and recycling, summery report, International conference, *Scope News letter no. 56*, **2004**.
- [10] Pramod N.K., Viswas B.G. and Shashikant R.K., *Der chemical Sinica*, **2011**,2, 4, 219-228.
- [11] Suthar K J , Chokshi NP ,Study on MAP process at laboratory scale for the removal of NH₄-N. International conference on current Trend in technology, **2011** NUiCONE.
- [12] Nagendra K.C. and Ran K.T., *Advances in Applied Science Research*, **2011**, 2,5,211-212.
- [13] BhavasanD.S., *Advances in Applied Science Research*, **2012**,3,3,1250-1254.
- [14] Vinesh V.R. and Puranik S.A, *Advances in Applied Science Research*, **2012**, 3,3 12791-12800.
- [15] Milan M. and Oza B.N. *Der Chemica Sinica* **2011**, 2,4, 244-251.
- [16] Max S.P. and Klaus D.T. “Plant Design and Economics for chemical Engineers”, **2002**, 5th edition.
- [17] Etter B., Tilley, Khadk R. , Udert K.M. *Water Research*, **2011**, 45, 852 – 862.