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## Nutrient Recovery from Sewage Wastewater and Bittern as Precipitated Struvite Using Zeolite and Activated Carbon as Adsorbent

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### ABSTRACT

Removal of nutrients such as ammonium and phosphate ions by natural or synthetic zeolite has been studied on lab and pilot scales using an orbital shaker and mechanically stirred batch system respectively. Natural Zeolites are abundant and low cost resources. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolite has been widely used as adsorbents in separation and purification processes in past decades. The aim of the present study is to investigate adsorption and desorption behavior of Zeolite and activated carbon in removal of ammonium and phosphate from sewage wastewater (SWW). The lab scale was studied for the direct precipitation of struvite by adding bittern and crystallization of final product. On The pilot scale study the adsorbed/desorbed ammonium and phosphorous from 100 liter of (SWW) on Zeolite were precipitated by adding bittern as low cost source of magnesium ion. The Langmuir equation was fitted to the data points as 1<sup>st</sup> order model for Zeolite and activated carbon as adsorbents for both ammonium and phosphorous ions with ( $R^2 = 0.859$ ,  $R^2 = 0.9848$ ) and ( $R^2 = 0.9995$ ,  $R^2 = 0.6928$ ) respectively. The Scanning Electron Microscope (SEM) and X-Ray diffraction (XRD) were used to identify the morphology and the chemical composition of the struvite Fertilizer. A Preliminary Techno – Economic study was evaluated for pilot scale struvite production. The mass balance was studied for lab scale struvite precipitated.

**Keywords:** zeolite, adsorption, struvite wastewater, Langmuir Isotherm.

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## INTRODUCTION

With the increased awareness and understanding of the deleterious effects of nutrients the authorities have introduced stringent laws restricting nutrient discharges from both wastewater treatment facilities and other point source contributors, and hence efficient removal of nutrients is now required. The traditional solution to the problem of ammonium removal is biological treatment and there have been numerous research devoted to the various aspects of the nitrification/ de-nitrification process. Despite the effectiveness of biological systems, they require large reactor volumes or areas, and hence high capital costs due to slowness of the biological conversion process for nutrient ammonium [1]. The application of zeolite as an ion-exchanger for ammonium removal or recovery is one of the effective technologies that have received considerable attention in recent years. Zeolites are very effective in the removal of ammonium, as has been demonstrated in numerous studied worldwide which have used natural zeolite from many different deposits [2 – 7]. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treatment and the success of the technique depends on the development of an efficient adsorbent. Zeolites have been widely used as adsorbents of ions in wastewater treatment [8 – 11]. The use of natural zeolite for environmental applications is gaining new research interest mainly due to their properties and significant worldwide occurrence [12]. The removal of phosphate by adsorption is quite simple and convenient. Successful results were reported by various researchers [13]. Phosphate ions can be removed by ion exchange or physical adsorption on zeolite. The system was considered to be suitable because of low-cost media and energy saving [14]. Liquid bittern was used as a low cost source of magnesium for the removal of ammonium and phosphate ions from wastewater by precipitating in the form of ammonium magnesium phosphate  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  compound, also known as struvite [15]. Activated carbon and zeolite as ammonia adsorbents have been compared in fish cultures and both adsorbents were found to be effective on ammonia reduction, but zeolite was considered cheaper and easier to manage [16]. Technologies using carbon based adsorbents (activated carbon, fly ash, charcoal, etc.) are widely used in removal of phenolic acids from industrial wastewater [17]. However, little is known about the behavior of carbon based adsorbents in nutrient removal from domestic wastewater and separating it as a fertilizer has not been investigated before. The presence of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$  and  $\text{Mg}^+$  could reduce the uptake of ammonium onto zeolite. The order of ammonium ion over other cations was  $\text{Na}^+ > \text{K}^+ > \text{Ca}^+ > \text{Mg}^+$  while the presence of humic acid increases the uptake of ammonium [12]. About 23% of adsorbed ammonium could be desorbed by tap water and desorption is more pronounced during saturated conditions [13]. However natural zeolite after ammonium adsorption can be regenerated by Na or K ion exchange or by heat treatment for ammonium de-volatilization. Heavy metal ions in water supplies produce strong health problem and damage to plant and animals. The metal ion in sewage waste water systems has adsorption affinity to zeolite [14]. The aim of the present study was to optimize the recovery of P and N from sewage waste water in combination with struvite precipitation by liquid bittern and ammonia adsorption by zeolite. Langmuir adsorption isotherm was studied for ammonium and phosphorous too.

## MATERIALS AND METHODS

### Sewage wastewater analysis

Sewage wastewater samples were collected from the influent point of Zenin wastewater treatment station, Giza, Egypt. Characterization of the waste water involved the determination of  $\text{NH}_4$ ,  $\text{PO}_4$ , COD, TDS, conductivity, alkalinity and pH using HACH DR 2000 Spectrophotometer Table (1). The pH of wastewater samples were analyzed immediately after samples collection. The samples were collected in plastic containers and stored at 4 °C before analysis. Samples thereafter were used in batch experiments. The pH was adjusted by addition of 0.1m phosphoric acid. All parameters were analyzed in accordance with the Standard Methods for the Examination of Water and wastewater [18].

**Table 1: Characteristic of sewage wastewater samples**

Parameters	Average value
pH	7.7
TDS	910 mg/L
Conductivity	1.81 mS/cm
Ammonium	0.255 mg/L
Phosphate	20.77 mg/L
COD	730 mg/L
Ca	13.84 mg/L
Mg	11.36 mg/L
Hardness	25.19 mg/L

Liquid bittern was obtained from the El Nassr and Salt Company, Alexandria, as low cost of magnesium source, Table (2) shows Characteristics of liquid bitten used.

**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

The properties of adsorbents Zeolite (sodium Silicate Hydroxide  $\text{Na SiO}_2 \cdot 6\text{H}_2\text{O}$ ) and activated carbon used in the experiments were obtained commercially from the industries as discussed by [19].

The XRD and SEM analysis were used to confirm precipitated struvite and its morphology. A preliminary economic study was evaluated on the Pilot experiment for struvite precipitated from 100 liter sewage wastewater and desorbed from zeolite.

### Adsorption and precipitation tests

The experiments for struvite precipitation by ammonium uptake by zeolite were studied as adsorption / desorption. Different amounts of zeolite and activated carbon adsorption were studied for ammonium removal. Samples of 100 ml Sewage water were used for each batch with the following treatments: (0, 0.2, 0.375, 0.5, 0.75, 1, 1.5, 2) g/L sewage wastewater. The samples were left in beakers for 72 h at room temperature (20 °C) with short stirring using orbital shaker at 350 rpm for 15 min once daily. Researchers showed that sorption time of ammonium ion to zeolite was 15 min [20]. The mineral zeolite chemical content ( $\text{Na Al}_2 \text{SiO}_9 \cdot 9\text{H}_2\text{O}$ ,  $\text{SiO}_2$  and  $\text{NaSiO}_2 \cdot 6\text{H}_2\text{O}$ ) and it was used without pretreatment or previous activation. The activated carbon (AC) used was high quality commercial charcoal. After 72 h the supernatants from one set of beakers were decanted and collected for chemical analysis. The supernatant were analyzed for total –P, total –N, TDS and conductivity Table (3).

**Table 3: Supernatant analysis using different dose of Zeolite**

Zeolite dose (g/L)	Conductivity (mS/cm)	TDS g/L	$\text{NH}_4$ (mg/L) in supernatants	$\text{PO}_4$ mg/l in Supernatants
0	1.82	0.91	0.255	20.769
0.2	1.12	0.56	0.1225	23.846
0.375	0.94	0.47	0.15	23.846
<b>0.5</b>	<b>0.98</b>	<b>0.49</b>	<b>0.141</b>	<b>5.385</b>
0.75	0.96	0.48	0.848	15.385
1	0.92	0.46	0.14	19.231
<b>1.5</b>	<b>0.91</b>	<b>0.46</b>	<b>0.121</b>	<b>16.923</b>
2	0.95	0.47	0.105	11.538
4	1.08	0.45	0.076	

## RESULTS AND DISCUSSION

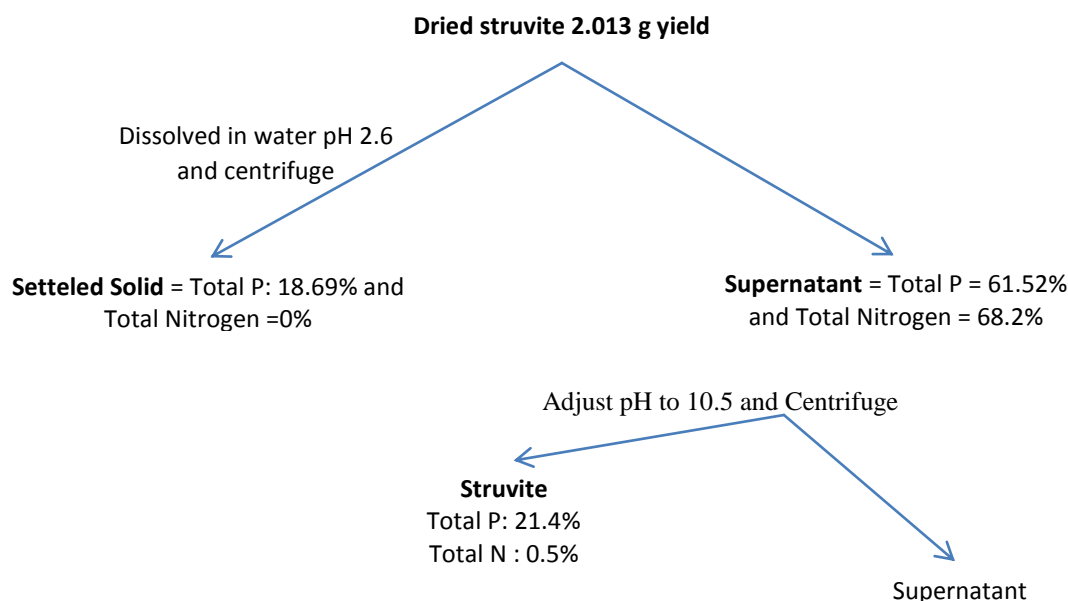
### Total ammonium and phosphorous reduction

The concentration of total phosphorous and total ammonia in supernatants are presented in Table (3) Desorption of adsorbed ammonia was investigated by two experiments carried out at room temperature using tap water as leaching agent[21]. After then the pH was adjusted to 9.5 using 0.1N NaOH and addition of liquid bittern precipitated struvite as magnesium ammonium phosphate hexa-hydrated. Our results show that maximum reduction

of ammonium in sewage wastewater was 61% and 59.3% using zeolite and activated carbon respectively. While maximum reduction of phosphorous in sewage wastewater was 74% and 88.7% using zeolite and activated carbon respectively.

**Mass balance and purification of struvite precipitated on lab scale:**

During struvite crystallization, large amount of solids settling down to the bottom of the reactor along with the crystals and can interfere with the precipitation process. Therefore, getting high purity struvite is unfeasible. In the present study, to get the pure struvite, a feasible method was designed and properties of sediment collected and the purified struvite were analyzed using XRD. The purification process is given in Fig (1). The crystalline struvite is shown in Fig (2) and chemical composition in XRD pattern Fig(4) and Fig(5) .



**Figure 1: Crystalization of struvite precipitated on lab scale.**



**Figure 2: Image of the purified struvite after precipitation from sewage waste water and dark residual soids.**

Fig(3) shows the XRD pattern of precipitated struvite without purification and indicating that struvite as major product. Fig (4) shows the XRD pattern the dark separated solids during purification of struvite. The major content is struvite and nearly equal to the Calcium phosphate

hydroxide Hydrate. Fig (5) shows the XRD pattern and the composition of major pure crystalline struvite as  $Mg NH_4 PO_4 \cdot 6(H_2O)$  and manor  $Mg_3(PO_4)_2 \cdot 22 H_2O$ .

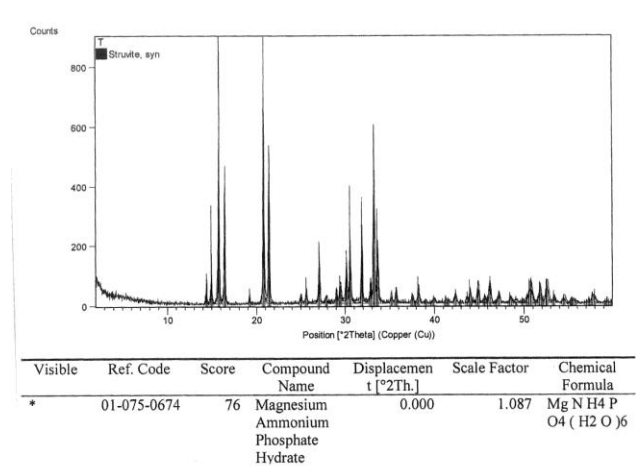


Figure 3: XRD pattern of struvite precipitated from sewage waste water.

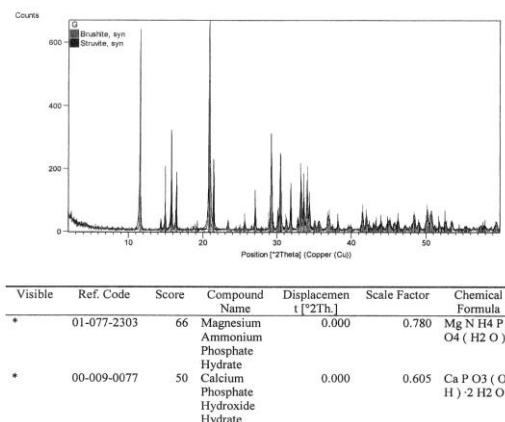


Figure 4: XRD pattern contents of gray solid separated from yield precipitated from sewage waste water.

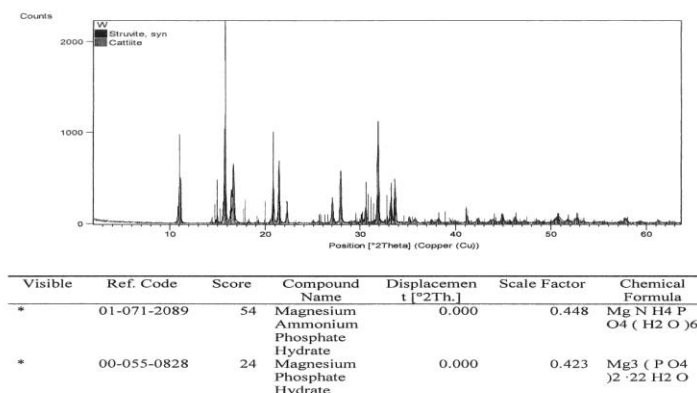


Figure 5: XRD pattern contents of crystalline struvite separated from yield precipitated from sewage waste water

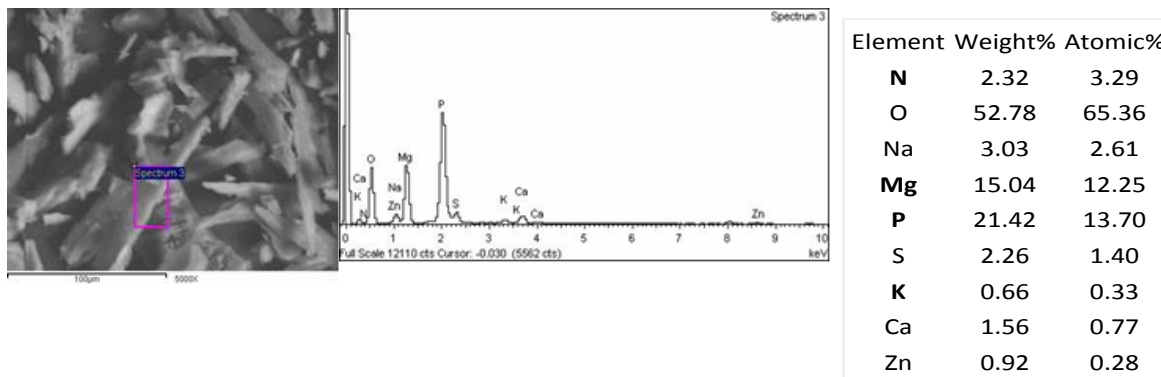


Figure 6: SEM image and EDCs analysis for crystalline struvite precipitated from sewage wastewater

Fig (6) shows SEM and EDCs analysis for pure white crystalline struvite. The chemical composition of the purified struvite contains nitrogen and high phosphorous and magnesium 2.32%, 21.42% and 15.04% respectively. Struvite  $Mg NH_4 PO_4(H_2O)_6$  product precipitated at sewage wastewater of 46.28% crystallized and 36.31% phosphate salts).

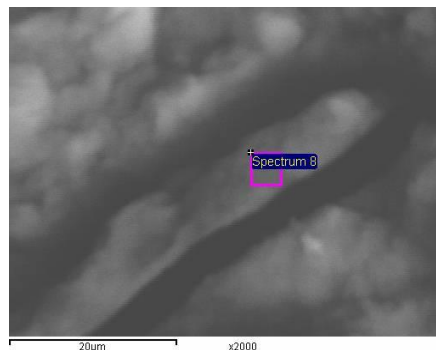


Figure 7: SEM image showing elongated crystal for struvite precipitation on pilot scale

### Preparation of Struvite from sewage Wastewater on Pilot Scale

#### 1- Adsorption Step

To 100 liters of sanitary wastewater ( $NH_3 = 0.08$  mg/L) and ( $PO_4 = 998.46$  mg/L) add 150 gm of zeolite, then mix at low stirring rate (250 rpm) for 30 minutes then let overnight to adsorb ammonia on zeolite.

Stirring followed by settling overnight were repeated three times.

After that the clear solution was siphoned ( $\approx 80L$  of  $NH_3$  conc = 0.02 mg/L g/L) and  $PO_4$  conc=440.25mg/L.

#### 2- Generation Step.

To the zeolite after absorbing ammonia add 60 L of fresh tap water then stir for 15 minutes and let to settle overnight.

#### 3- Filtration

The slurry from step 2 was filtered to take the zeolite on the filter cloth and the clear filtrate.

#### 4- Precipitation of Struvite

To the filtrate (66L. of  $NH_3$  0.02mg/L,  $PO_4$  440mg/L pH = 7.8) add about 2800 mL of sodium hydroxide solution (1N) to elevate the pH to  $\approx 9.72$ .

Then add 1.1L of bittern ( $Mg^{++}$  75 g/L) and stir for 15 minutes and let to settle down overnight.

Filtrate the precipitated struvite, dry it then weigh and analyze on XRD to determine its purity and SEM to show crystals shape.

#### 5- The regenerated zeolite with tap water was then added to previous siphoned 80 liter and stirred for 30 min and let to settle overnight (twice).

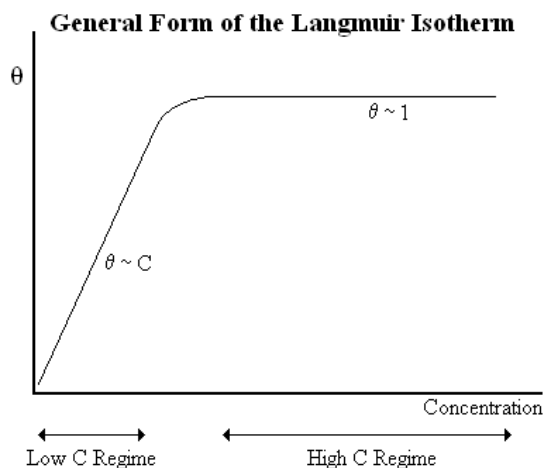
#### 6- Step (2) and step (3) were repeated again for more generation of white crystalline struvite.

#### 7- The total yield of precipitated struvite is 360.4 g/100 L sanitary wastewater. Fortunately we gained more than 1 g/L i.e. an economic precipitate of slow release fertilizer.

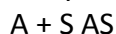
In the pilot scale precipitation of struvite at high ammonium concentration of sewage wastewater more than 90% of the adsorbed ammonia was recoverable as exchangeable ammonium. This indicates that adsorption of ammonia as (fixed) ammonia takes place prior to adsorption onto sites of cation exchange [16].

### Ammonium and phosphorous Adsorption Isotherms

Langmuir adsorption isotherms were determined for the study of zeolite and activated carbon as adsorbents for ammonium and phosphorous. Adsorption ability to reduce ammonium and phosphorous losses in the experiment were studied according to the following isotherm



The chemical reaction for monolayer adsorption can be represented as follows



Where, AS represents a solute molecule bound to a surface site on S. The equilibrium constant  $K_{ads}$  for this reaction is given by

$$K_{ads} = \frac{[AS]}{[A][S]} \tag{Eq. 1}$$

[A] Denotes the concentration of A, while the other two terms [S] and [AS] are two-dimensional analogs of concentration and are expressed in units such as mol/cm<sup>2</sup>. The principle of chemical equilibrium holds with these terms. The complete form of the Langmuir isotherm considers (Eq.1) in terms of surface coverage  $\theta$  which is defined as the fraction of the adsorption sites to which a solute molecule has become attached. An expression for the fraction of the surface with unattached sites is therefore (1 -  $\theta$ ). Given these definitions, we can rewrite the term [AS]/[S] as

$$\frac{[AS]}{[S]} = \frac{\theta}{(1 - \theta)} \tag{Eq. 2}$$

Now we express [A] as C and rewrite (Eq. 1) as:

$$K_{ads} = \frac{\theta}{C(1 - \theta)} \tag{Eq. 3}$$



Rearranging, we obtain the final form of the Langmuir adsorption isotherm:

$$\theta = K_{ads} C / 1 + K_{ads} C \quad (\text{Eq. 4})$$

IF we define  $Y$  as the amount of adsorption in units of moles adsorbate per mass adsorbant, and  $Y_{max}$  and the maximal adsorption, then:

$$\theta = Y/Y_{max} \quad (\text{Eq. 5})$$

And the isotherm can be expressed as:

$$C/Y = 1 / Y K_{ads} * Y_{max} + C / Y_{max} \quad (\text{Eq. 6})$$

At lower concentrations, an alternate isotherm developed by Herbert F. Freundlich frequently describes the data better. The Freundlich Isotherm is:

$$Y = k C_{1/n} \quad (\text{Eq. 7})$$

Where, the Freundlich parameters  $k$  and  $n$  are empirically determined. A plot of  $\log Y$  vs.  $\log C$  allows for a determination of these parameters [17].

### Application of Langmuire and Freunlich equation

According to equation [7] our results shows that Zeolite had both high affinity for ammonia and high adsorbtion capacity of (0.15mg/L) at ammonia removal = 58% and adsorption capacity of (15 .39 mg/L) at phosphate removal = 74.07%. Fig (8) and Fig (9) respectively.

Activated carbon had nearly the same adsorption capacity of 0.149 mg/L for ammonium adsorption concentration and 18.46 mg/L for phosphorous adsorption as illustrated in Fig (10) and Fig (11). The straight line in the Figures illustrates the initial low concentration of both ammonium and phosphorous in sewage wastewater effluent samples. When Comparing zeolite adsorption with activated carbon adsorption affinity for recovery of ammonium as nutrient, zeolite shows better and easier as ammonium adsorbed can be recovered in tape water. The recovered ammonium is precipitated as struvite fertilizer by adding NaOH 1 normal till pH value (9.5 – 10) and bittern as source of low cost magnesium.

### The Langmuire and Freundlich Kinetic model fittings

As the concentration of both ammonium and phosphorous were low in the initial sewage waste water effluent, the Langmuire and Freundlich model fitted to the data points using linear regression and first order kinetic model as shown in Fig (12) , Fig(13), indicating zeolite adsorbtion and Fig (14) and Fig(15) illustrating activated carbon adsorption. The  $R^2$  fitted



(0.859 and 0.9848) for zeolite and  $R^2$  fitted (0.9995 and 0.6928) for activated carbon. This indicates that zeolite has better affinity than activated carbon for ammonium recovery.

### **Preliminary Techno – Economic Evaluation for Struvite Production from Sewage Wastewater**

Simulation and basic engineering of struvite production for proposed capacity 320 tons/year (1066.8 kg /day or 355.6 kg/ shift) has been developed. The simulation Includes the following reaction, mixing, settling, siphoning, regeneration. Equipment's used are mixer, settler and filter, vacuum dryer and packing unit as shown in flow sheet Fig (16).

So total selling price =  $3000 \times 320 = 960,000$  L.E

Total production cost =  $2182 \times 320 = 698,225$  L.E

Profit =  $960,000 - 698,225 = 261,775$  L.E

Annual percent return on the total initial investment (excluding income taxes)  $r = 52 \%$

$r = (\text{annual net profit}) / (\text{fixed capital investment} + \text{working capital}) = 261,775 / (453,420 + 45,342)$

### **Payout Period ( $\tau$ )**

Payout period is defined as the minimum length of time theoretically necessary to recover the original capital investment in the form of cash flow to the project, based on total income minus all costs except depreciation. Generally, for this method, original capital investment means only the original, depreciable, fixed capital investment, and interest effects are neglected.

Therefore:

$$\tau = \frac{FCI}{x + y}$$

Where,

FCI = 453,420 L.E

x = average profit per year, LE 261,775

y = average depreciation per year, 10,000 L.E

$\tau = 1.668$  years.

### **CONCLUSION**

The zeolite used without previous treatment has efficient sorption performance and high simultaneous removal effects of ammonium and phosphates. The SEM, EDS and XRD analysis show the presence of nitrogen, magnesium, phosphorous and potassium in the struvite product where P and Mg as major contents N and K appeared in lower contents. The ammonia and phosphate data could be well fitted by the Langmuir isotherm model and the sorption of

zeolite to ammonium and phosphates process involves rapid adsorption. The preliminary Techno – Economic Evaluation for Struvite Production from Sewage Wastewater showed economic production especially when precipitated in tap water.

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