Phosphorus Recovery Technologies for Municipal and Industrial Wastewater：Taiwan's Perspective

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Abstract

The combination of phosphate and ammonium rich streams for struvite recovery from municipal wastewater by conventional enhanced biological nutrient removal process following the fluidized bed crystallization (FBC)unit has been developed and applied in Taiwan. FBC uses silicate sand as a carrier to recover metal salts or inorganic ions from TFT-LCD, and the semiconductor industry also has been demonstrated in many full-scale facilities. Crystals that are large in size(3~5mm), have low water content, high purity, less heavy metal contamination and sufficient hardness are necessary to meet the requirement of commercial fertilizer spreader and marketing. In Taiwan, fertilizer recovered from sewage or industrial wastewater is forbidden in some local agencies due to the concern about the accumulation and transport of hazardous impurities. This paper presents the practical experiences of the applied technologies in both municipal and industrial aspects.

keywords：phosphorus recovery, wastewater, fluidized bed crystallization, struvite.

1. Introduction

The struggle over industrial water availability is set to shape a new turning point in the development of high-tech industries in Taiwan. Due to an industrial clustering effect, the number of giant regional water consumers has soared. Of the existing 91 industrial parks that are under development, 48 shall have water demand of over 10,000 m^3/day in 2031, and 10 of them will need more than 100,000 m^3/day. The water recycling rate in the main industrial parks was approximately 64% in 2009. The goal is to reach more than 75% in 2031. In addition to water stress, wastewater management practice contributes to nutrient imbalances. We acknowledge a new paradigm focusing on what can be recovered from wastewater in stead of what must be removed from it. Reclaimed water as a major driving force may make phosphorus recovery possible and economically feasible.

2. Process Selection

2.1 Biological Processes are Necessary for Municipal Wastewater

A large part of phosphorous in influent of municipal wastewater is organic combined complex, which are not ready to be precipitated or crystallized. During conventional secondary biological process, microorganisms break down complex and take up phosphorous for cell growth, which is eventually released into the liquid again after biosludge digestion in a simple form as $PO_4^{\equiv}$ ion. That's why as we understand that directly precipitate from influent can only recover 30-50% phosphorus in the municipal wastewater, but via biological aerobic and anaerobic digestion process, the phosphorus recovery can reach 70-95%.

2.2 Struvite crystallized by fluidized bed reactor

Struvite（$MgNH_4PO_4.6H_2O$, MAP）is commonly found in wastewater. The formation of struvite crystal from anaerobic digester liquids, which is characterized as high [PO_4^{-3}] and [NH_4^+] concentration, is thermodynamically feasible in most of municipal wastewater treatment plants. The reactor design is dependent on the morphology and density needed of the final product. The fluidized bed crystallization（FBC）can grow crystals to 3~5mm in diameter with much greater hardness and less water content and much higher purity（less heavy metals impurities is very important to be accepted using as fertilizer）than those products from selective precipitation process.

2.3 Operation Parameter

The key operation parameter for FBC is Super Saturation Ratio（SSR）, SSR is defined as Equ.（1）

$$SSR=Ps/Ps^{eq} \quad (1)$$

Where Ps is a conditional solubility product, and

simply defined as the product of these three measured concentrations.

$$Ps=[Mg^{+2}]\,[NH_4^{+}\text{-}N][PO_4^{-3}\text{-}P] \quad (2)$$

Ps^{eq} is defined as the equilibrium conditional solubility product.

$$Ps^{eq}=\frac{Ksp}{(\alpha_{Mg^{+2}}\gamma_{Mg^{+2}})(\alpha_{NH4^{+}}\gamma_{NH4^{+}})(\alpha_{PO4^{-3}}\gamma_{PO4^{-3}})} \quad (3)$$

Where Ksp is solubility product for struvite, α is ionization fraction and γ is activity coefficient for the respective ion species. SSR＞1 indicates the potential for struvite formation. SSR＜1 reveals that the system is undersaturated and results in no potential for sturvite formation. Due to the fact that Ps^{eq} is highly correlated with pH value and the operation range of SSR is relatively small（less than 10）, it is recommended that the ideal metastable zone to gain large size and stable growth of the struvite crystal can be obtained within a range of SSR values between 3 and 5.〔1〕

3. Case Examples

3.1 UASB / BioNet / MBR Patented Units

UASB（upflow anaerobic sludge bed）technology was developed by ITRI（Industrial Technology Research Institute, Taiwan）in 1980. More than 50 full-scale UASB reactors have been demonstrated. Table 1 indicates the major case examples. Table 2 shows UASB can be applied in TFT-LCD plants.

ITRI's know-how and patents include: Mechanisms of Anaerobic Microbial granulation；Extracellular polymer and granulation rate；Starvation start-up operation strategy to reduce the start-up period from 3 months to 3 weeks .UASB incorporated by BioNet（fixed-film sponged carrier）and MBR（membrane bioreactor）can be applied in municipal wastewater treatment. Non-Woven fiber MBR is the unique and most successful solution developed by ITRI to overcome the membrane fouling and to increase the flux rate. UASB with BioNet and/or MBR is good for the break down organic compound, digest biosludge and release the orthophosphate and then ready for struvite formation.

3.2 FBC Patented Technologies

ITRI's know-how and patents on the Fluidized Bed Crystallization（FBC）process include: Reactor and process control； Influent flow distribution design；Crystal growth control.（US 6,235,203；6,210,589；NL 1004621,1011698,1014191；CN ZL96213888.6；TW 089519, 122668, 143243, 161598, 168932）

Table 3 summarizes the applications. Fig 1 is a picture of 6000 ^{m3}/day water softening plant by FBC process. Fig 2 is the crystal obtained from FBC process of different wastewaters.

3.3 Selective Precipitation for Industrial Wastewater

Wastewater from the semiconductor industry contains high levels of $[F^{-}]$and$[SO_4^{-2}]$、$[PO_4^{-3}]$、$[NH_4^{+}]$ in wet etching process. Calcium reacts with both phosphate and fluoride, the calcium phosphate$[Ca_5(PO_4)_3OH]$cannot be obtained in pure form. Magnesium salts（$MgCl_2$）can be a good solution in recovering$[PO_4^{-3}]$ from waste stream, knowing that they have low reactivity with fluoride. Therefore, the selective precipitation processes for wet etching wastestream include：

Pretreatment（pH＜3.0）：

Selective precipitation by $Ca(OH)_2$and $CaCl_2$ to recovery CaF_2 and remove metal ions.

Selective precipitation（pH at 3~10）：

Selective precipitated by $MgCl_2$ to recovery $[PO_4^{-3}]$ in different forms.〔2〕

Table 1: UASB（ITRI）Applications

Factory name	Reactor Size（m^3）	Type of Wastewater	COD-in（mg/1）	CODr（%）
Asia Chemical Co.	1,000	Chemical processing	9,000	98
Yilan Wine Plant.（total 7 plants）	3,000	Fermentation and distillation	4,000-30,000	90
Hualon Toufen Ⅲ	600×2	Textile industry	5,000	90
Hualien distillery	1,300	Distillation	10,000	90
Hualon Malaysia Ⅰ	600×2	Textile industry	5,000	90
Hualon Malaysia Ⅱ	600×2	Textile industry	5,000	90
Dahin Co./Chuan Hsing plant	500	Chemical processing	8,000	≧70
Taiwan petrochemical	800	Chemical processing	12,000	80
Dahin Co.	900	Chemical processing	8,000	80
President Enterprises Co. Ⅱ	900×2	Food processing	2,500	90
Der-Yien Paper Industry	900×2	Pulp and paper	7,000	80
Chang Chun Petrochemical Ⅱ	1350×2	Petrochemical industry	3,000	≧70
Kinmon distillery	1,000	Distillation	3,000	90

Table 2: UASB for TFT-LCD plants

Factory name	Reactor size（m^3）	Type of wastewater	COD（mg/L）
Toppoly Optoelectronics	1,760	TFT-LCD（MEA,BDG,TMAH）	8.000
Chi Mei Optoelectronies Ⅰ	900	TFT-LCD（MEA, DMSO, TMAH）	1.000
Chi Mei Optoelectronies Ⅱ	400	TFT-LCD（MEA, DMSO, TMAH）	1.000

Fig.1 6000m^3/day FBC Water Softening project for Taiwan Water Corporation

Fig. 2 Colorful crystals discharged from FBC system for treating different wastewaters.

Table 3: FBC applications

Type of industry	Function	number of full-scate operation
Semiconductor	F^-removal	5
TFT-LCD	F^-removal	2
TFT-LCD	NH_4^+ removal	2
Water Softening	Ca^{+2}removal	1
Petrochemical	Ca^{+2}removal	1
Printed Circuit board（PCB industry）	Water reuse heavy metal removal	1

Table 4：Characteristics of semiconductor waste stream

Components	Concentration（mg/L）
Fluoride（F^-）	800-1000
Sulfate（SO_4^{-2}）	500-650
Phosphate（PO_4^{-3}）	100-120
Ammonium（NH_4^+）	20-30

Table 4 shows the characteristics of the wet etching wastes from semiconductor plants. Magnesium salts have low reactivity with fluoride, therefore, can be a good separator for phosphorus from fluoride ions. $MgCl_2$ is more effective than MgO. High concentration of fluoride is also a cautious factor. The solubility of CaF_2at pH＝2.0 is about 65 mg/L. Therefore, around 95％ of the influent of fluoride（F-:1000mg/L）will be precipitated as CaF_2 if Ca^{+2} is sufficient. At pH＝3.0, reversely, the solubilities of Fe（OH）$_3$, Ni（OH）$_2$and Cr（OH）$_3$ are all very high, and can be separated and get high quality of CaF_2.

4. Conclusions

4.1 Biological nutrient removal process has become an established technology in municipal wastewater treatment facilities. ITRI's patented units such as BioNet, MBR and UASB, make the control of sludge age and mass ratio easier and more efficient than other alternatives. The combination of phosphate and ammonium rich streams after biological processes is suitable for struvite（$MgNH_4PO_4 \bullet 6H_2O$）recovery followed by the fluidized bed crystallization unit（FBC）.

4.2 For industrial wastewater, source separation is the key concept to design a practically feasible system. Selective precipitation on-site to recover fluoride and phosphate compound respectively as primary sludge-cake like products which can then be further processed in a centralized off-site facility to meet different quality requirements. Magnesium salts have low reactivity with fluoride, therefore, can be a good separator for phosphorus from fluoride ions. Selective precipitation of phosphorus from semiconductor and TFT-LCD wet itching waste streams seems a promising approach. Due to the variety of the high-tech processes or unit operations, it is difficult to make generalizations that can be applied to all systems. Theoretical chemistry calculation and laboratory testing are demanded for process control.

4.3 Industries need to have a stable water supply system. Reclaimed water has recently come to be an option in Taiwan, due to the shortage of water supply of around 50,000^{M3}/day for an expanded semiconductor manufacture case. Desalination seawater contains trace component such as boron may not be suitable to semiconductor process. Integrating point of discharge（POD）, point

of source（POS）, and point of use（POS）management really pushes top managers to reconsider the cost of water and nutrients recovery. In this scenario, phosphorus recovery may be considered as economically feasible.

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6. References

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