

# Study on Release Characteristics and Recovery of Nitrogen and Phosphorus during the Anaerobic Fermentation of Excess Sludge

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**Abstract.** Ammonia nitrogen and phosphate are produced from activated excess sludge under anaerobic conditions, and will cause eutrophication upon release to the environment. A study of sludge from a eutrophication was carried out, to obtain knowledge of the nitrogen and phosphorus release patterns of the excess sludge during anaerobic fermentation and the recycling efficiency of both nitrogen and phosphorus, by adding magnesium salt and alkali solution to the supernatant liquors. The results showed that the concentration of ammonia nitrogen and phosphate of the supernatant liquors continued to increase during the process of anaerobic digestion, and both reached a maximum in 12 days, at 41.56mg / L and 47.02 mg / L respectively. By adding magnesium salt to the supernatant with c(Mg): c(P) = 1.1:1, adjusting pH value to 9.0 ~ 9.5, phosphorus recovery rate reached up to 95.0%, while the recovery rate of ammonia was 47.4%, resulting in the formation of a sediment of magnesium ammonium phosphate, or MAP, which may be used as a high-quality fertilizer.

## 1. Introduction

Environment problem is one of the major problems faced by mankind currently. Urban production and life sewage discharge is increasing with the speeding up of urbanization process. The eutrophication problem of water bodies is becoming more and more serious. Nitrogen and phosphorus are main reasons of eutrophication in slow flow water bodies such as lakes, reservoirs, bays, etc. [1]. After nitrogen and phosphorus in sewage flow into water bodies, blooms of algae, serious oxygen deficiency of water body, fish death and water body ecological function degradation are caused. Finally, the water body is in a state of eutrophication. Water bloom and red tide of water bodies also can be caused more severely, thereby directly threatening human health [2]. Water pollution, especially water body eutrophication, has become an important influencing factor of economy development in China [3]. Meanwhile, phosphorus is a non-renewable resource in the natural cycle of phosphorus. It is estimated that phosphorus resources on the earth will be used up within 60-130 years at the current mining speed [4]. Therefore, the loss of phosphorus belongs to a waste in the aspect of resources. If recycling measures are not adopted, phosphorus will be used up eventually. The loss of phosphorus can aggravate the burden of natural environment in terms of environmental protection, which will damage the environment eventually.

Currently, urban sewage treatment plants in China mostly adopt biological nitrogen removal technology to control the nitrogen and phosphorus of the discharged water. However, the excess sludge



produced in biological nitrogen removal system can produce a large number of rich phosphorus liquid in sludge concentration, dewatering, anaerobic digestion and other disposal process. The mass concentration of phosphorus can be up to more than 100 mg/L [5]. The above rich phosphorus liquid usually flows back into the initial end of the sewage system. The sewage factory phosphorus load can be increased by 10% ~ 15%, thereby directly affecting the operation efficiency of wastewater biological treatment system.

Domestic and foreign scholars have done a lot of research work in response to the recycling and utilization of nitrogen and phosphorus in wastewater, especially the recycling and utilization of phosphorus. Great progress has been made in the aspects of model, mechanism, etc. The research on the production process of phosphorus recovery is relatively mature in the Netherlands and Japan with productive application examples [6-7]. Research of the field is still in its infancy in China. Since some scholars begin to pay close attention to the research field, literature of introducing domestic related research theory and technology appears in China [8-9], Wang Shaogui, etc. carried out lab-scale test in the form of recovering phosphorus by struvite [10], Chen Yao, etc. conducted experiments of recovering phosphorus in the form of calcium phosphate [11], some scholars study synchronous recycling and utilization of nitrogen and phosphorus in wastewater [12-13], Tong Juan et al. studied the influence factor of phosphorus removal by excess sludge hydrolysis acidizing fluid, thereby determining the optimum pH value, magnesium phosphorus ratio, etc. of struvite recycling method, Bi Dong et al. studied phosphorus release rule, measurement relationship, etc. of rich phosphorus excess sludge anaerobic storage process. However, the research on concrete release trend of nitrogen and phosphorus in anaerobic fermentation of excess sludge is rarely reported. In the paper, the excess sludge in Hefei Wangxiaoying Sewage Treatment Plant is regarded as the research object in order to determine the specific release trend of nitrogen and phosphorus in sludge during sludge anaerobic fermentation, and the release proportion of nitrogen and phosphorus. Meanwhile, the recovery efficiency of nitrogen and phosphorus in sludge fermentation supernatant is studied by using MAP ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , commonly known as guano) which is frequently studied in the industry.

## 2. Methods of Test and Analysis

### 2.1 Materials and Methods

The excess sludge for experiment is taken from the sludge reflux well of Hefei Wangxiaoying Sewage Treatment Plant. Wangxiaoying Sewage Treatment Plant adopts modified oxidation ditch treatment process, which has good phosphorus removal effect.

The obtained excess sludge has the following initial features: pH 6.84, MLSS 9715 mg/L, MLVSS 3941 mg/L, SCOD 135 mg/L, TC 3730mg/L, IC 2420 mg/L, TOC 1307mg/L, TC 3730 mg/L, TP 81.49 mg/L,  $\text{P-PO}_4^{3-}$  1.52mg/L, TN 77.68mg/L and  $\text{N-NH}_4^+$  0.75mg/L, wherein pH,  $\text{P-PO}_4^{3-}$  and  $\text{N-NH}_4^+$  are sludge supernatant indicators. TC refers to the sludge concentration which is converted after C content in filtered and dried solids is measured.

The excess sludge obtained from the sludge well is evenly placed in several 500mL brown anaerobic digestion bottles. They are divided into two groups, which are sealed. The bottles are shaken regularly every day, thereby the sludge can be mixed evenly. Meanwhile, the anaerobic digesting bottles are shaken evenly temporarily before each sampling. The sludge samples in the bottles can be mixed evenly, and then the sludge can be sampled. The samples are centrifuged for 10 min by a centrifugal machine firstly, which are filtered by 0.45  $\mu\text{m}$  microporous membrane filter vacuum filter method. The ammonia nitrogen ( $\text{N-NH}_4^+$ ) and soluble reactive phosphate ( $\text{P-PO}_4^{3-}$ ) concentration in two groups of filtrate are analyzed respectively. Its average value is regarded as the final concentration.

The sludge is sampled at time interval of 1.5, 3, 4.5, 6, 7.5, 9, 10.5, 12, 21, 24, 36 and 48h respectively in the initial 2d of experiments. The above method is adopted for centrifuging and filtering. Then the concentration of ammonia nitrogen and phosphate in the filtrate is measured. The tendency chart (figure) 1 of ammonia nitrogen and phosphate concentration change with fermentation time within 48h is drawn. Then, the ammonia nitrogen and phosphate concentration in the filtrate is measured. The measurement

time interval is suitably prolonged. The concentration change tendency chart (figure 2) within 17d is drawn.

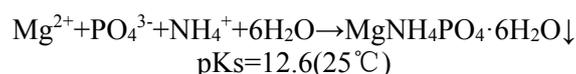
## 2.2 Analytical Methods

PH is determined by a pH meter. TC, IC, TOC and TN are measured by a total carbon and total nitrogen analyzer (multi N/T 2100). N-NH<sub>4</sub><sup>+</sup> is determined by Nessler's reagent colorimetric method. P-PO<sub>4</sub><sup>3-</sup> is measured by a molybdenum antimony spectrophotometer. The total phosphorus in sludge is dissolved by hydrogen peroxide. The supernatant in anaerobic fermentation sludge and solid phase are centrifuged by a centrifuge machine. 0.45μm microfiltration membrane vacuum suction method is adopted for separation. After the precipitation samples recycled in anaerobic fermentation liquid is dried, XRD detection is implemented to determine the main ingredients of precipitation.

## 3. Results and Discussions

### 3.1. Recovery Methods

The ammonia nitrogen and phosphate in supernatant are recycled with MAP precipitation method during anaerobic fermentation of excess sludge. MAP precipitation method can be applied for removing nitrogen and phosphorus in wastewater simultaneously. The MAP is commonly known as guano. Its chemical composition is MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O. English abbreviation is MAP. The solubility of struvite is extremely low, which is only 0.023 g/L at 0 °C. It has high potential market value as a slow-release fertilizer [19-21]. Mg<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub><sup>+</sup> form struvite according to the following reaction equation:



Alkaline conditions are required for various phosphate precipitation forms, because the solution pH value has great influence on the activity of NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>. It is reported that pH value scope required by struvite formation precipitation is 8.0–10.7, and satisfactory precipitation effect can be obtained when pH is 9.0 ~ 9.0 generally.

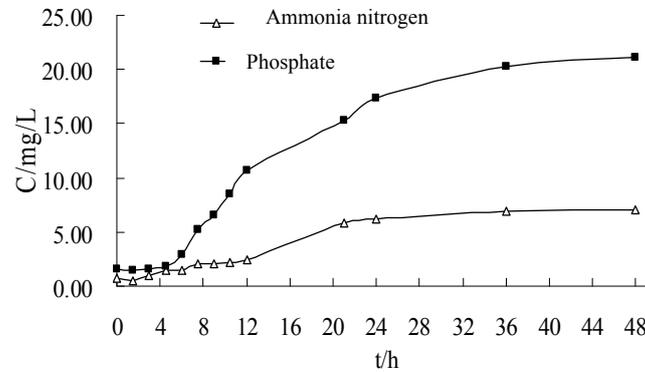
The mole ratio of Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>MAP for MAP formation is 1:1:1. In the experiment, we adopt the mode of feeding MgCl<sub>2</sub>·6H<sub>2</sub>O to realize synchronous recycling of ammonia nitrogen and phosphate in sludge fermentation supernatant.

### 3.2 Releasing Characteristics of Ammonia-nitrogen and Ortho-phosphate

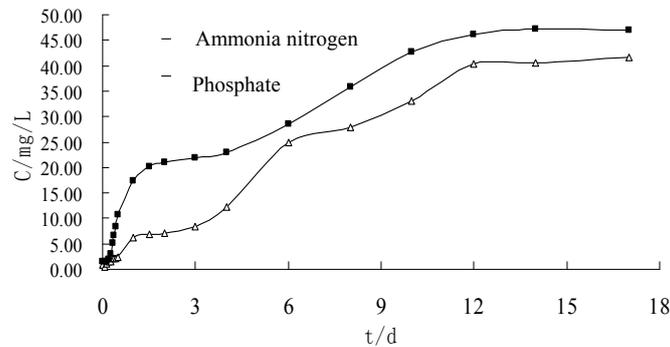
Figure 1 shows that the initial concentration of ammonia nitrogen and phosphate is low in anaerobic fermentation sludge supernatant. Reasons are analyzed. The concentrated sludge in the sludge well is sufficiently contacted with air, the the mobility is great, and sludge is oxygenated fully. The ammonia nitrogen is changed slightly within 12h at the beginning of fermentation, which is only increased by 1.70mg/L. The change speed is improved after fermentation for 12h, hwoever the overall concentration is increased slowly. The change rate of phosphate is limited in the first 4h. The change rate is prominently accelerated after fermentation for 4h. The increase speed is slowed after fermentation for 36h. Reasons are analyzed. The microorganisms have not enter into the anaerobic phase due to existence of dissolved oxygen at the beginning. After the dissolved oxygen is consumed, organisms start endogenous respiration because of the anaerobic environment. Cell tissues are decomposed to release nitrogen and phosphorus, thereby leading to increase of ammonia nitrogen and phosphate concentration in supernatant.

Figure 2 shows that ammonia nitrogen and phosphate change in supernatant are increased as a whole in the whole anaerobic fermentation process. Their concentrations reach the peak respectively at 12d or so, which tends to be stable. The peak concentration is respectively 41.56mg/L and 47.02 mg/L. Reasons are analyzed. Since 60% sewage source of Wangxiaoying Sewage Treatment Plant belongs to domestic sewage. Its nitrogen and phosphorus concentration is low. Though the adopted modified oxidation ditch

process has excellent denitrification and phosphorus removal effect, nitrogen and phosphorus concentration in the excess sludge is low.



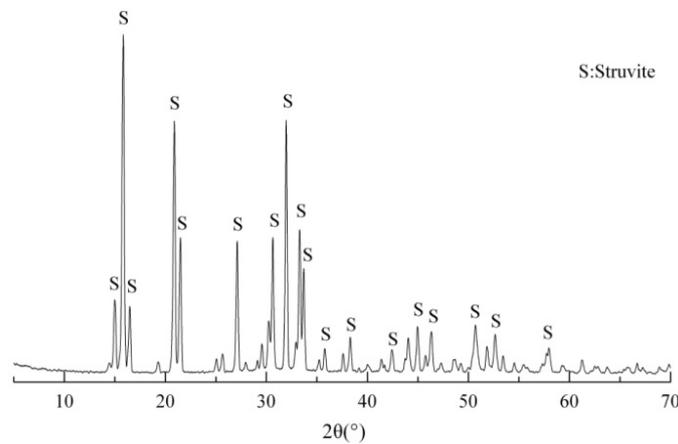
**Figure 1.** N and P change trend in excess sludge anaerobic digestion process (48h)



**Figure 2.** N and P change trend in excess sludge anaerobic digestion process (17d)

### 3.3 Analysis of Precipitation Sample

Samples are taken, and it undergoes vacuum suction filtering after being centrifuged. The concentration of ammonia nitrogen and phosphate in supernatant is measured.  $MgCl_2 \cdot 6H_2O$  is added according to the proportion of  $c(Mg):c(P) = 1.1:1.0$ . When NaOH solution is used for adjusting pH value to be 9.0-9.5, white precipitate is rapidly formed. The obtained white precipitate is collected for XRD test after being centrifuged and dried. The XRD figure of the precipitation products is shown in figure 3. After the figure is compared with a standard map, the main diffraction peaks in the map are MAP diffraction peaks. Therefore, it can be determined that the main component of white precipitate is MAP. The phosphate removal rate reaches 95.0% in sludge fermentation supernatant by calculation. The ammonia nitrogen removal rate reaches 47.4% (please see chart 1).



**Figure 3.** XRD figure of precipitation products

**Table 1.** Removal rate of nitrogen and phosphorus

	Before reaction (mg/L)	After reaction (mg/L)	Removal rate (%)
Ammonia nitrogen	41.56	21.84	47.4
Phosphate	47.02	2.35	95.0

#### 4. Conclusion

(1) The supernatant ammonia nitrogen and phosphate concentration show an overall increase change trend aiming at excess sludge in reflux well of Wangxiaoying Sewage Treatment Plant during anaerobic fermentation. Supernatant ammonia nitrogen and phosphate concentration respectively reach the peaks after anaerobic storage for 12d or so. The peak values of ammonia nitrogen and phosphate is respectively 41.56mg/L and 47.02 mg/L, which respectively account for 53.5% and 57.7% in total nitrogen and total phosphorus.

(2)  $MgCl_2 \cdot 6H_2O$  is added in supernatant during anaerobic fermentation of excess sludge. The pH is adjusted to 9.0~9.5 for recovering ammonia nitrogen and phosphate, wherein the recovery rate of the phosphate is 95.0%, and the recovery rate of ammonia nitrogen is 47.4%.

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