# Simultaneous Nitrogen and Phosphorus Recovery from Sludge-Fermentation Liquid Mixture and Application of the Fermentation Liquid To Enhance Municipal Wastewater Biological Nutrient Removal

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Recently, waste activated sludge (WAS) fermentation for short-chain fatty acids (SCFAs) production has drawn much attention because the waste biosolids produced in wastewater treatment plants (WWTP) can be reused, and the produced SCFAs can be applied to promote biological nutrient removal (BNR). Usually, after WAS fermentation, the fermentation liquid is separated and then the recovery of ammonium and phosphorus, which are released during WAS fermentation, is conducted to prevent the increase of nitrogen and phosphorus loadings to WWTP. As an alternative to the traditional process, this paper investigated the recovery of ammonium and phosphorus in the formation of struvite before sludge−liquid separation, and its positive effect on the following sludge−liquid filtration separation. First, the conditions for ammonium and phosphorus recovery from the WAS fermentation mixture were optimized by response surface methodology (RSM). Then, the effect of ammonium and phosphorus recovery on sludge filtration dewatering was investigated. With ammonium and phosphorus recovery, it was observed that the specific resistance to filtration (SRF), the capillary suction time (CST), and the sludge volume after filtration reduced by 96.9, 99.6, and 88.7%, respectively, compared with no ammonium and phosphorus recovered sludge. Third, the mechanisms for ammonium and phosphorus recovery significantly enhancing sludge dewatering capacity were investigated. The formation of struvite, the neutralization of $\zeta$ potential, the increase of magnesium ion, which was added during ammonium and phosphorus recovery, and the decrease of sludge polymeric substance caused the improvement of sludge dewatering. Finally, the fermentation liquid was used as the additional carbon source of BNR, and the nutrient removal efficiency was obviously enhanced.

## Introduction

Excessive nitrogen and phosphorus discharged from sewage and industrial wastewater is one key reason for eutrophication. Readily biodegradable carbon sources, such as short-chain fatty acids (SCFAs), are required for biological nutrient removal (BNR) in wastewater treatment plants (WWTP) (1). However, SCFAs are often insufficient for nitrogen and phosphorus removal in some areas, such as in South China, and external carbon source addition is required. Fermentation of sewage sludge can produce SCFAs, which can be used as the additional carbon source of enhanced biological nutrient removal (BNR) (2−4). After sludge fermentation, the separation process such as filtration is required to get the fermentation liquid from the fermented mixture. However, anaerobic treatment of sludge has been reported to significantly change the matrix of sludge flocs and particles, and consequently deteriorate sludge filtration dewatering capabilities (5).

In our previous investigations, it was reported that anaerobic fermentation of waste activated sludge (WAS) under alkaline conditions highly improved SCFAs production, and the fermentative SCFAs could be utilized as a better carbon source than acetic acid for biological phosphorus removal (4, 6). However, it was observed that it was difficult to separate the fermentation liquid from fermented sludge by either filtration or centrifugation. Another problem involved in WAS fermentation is that significant amounts of soluble ortho-phosphorus (SOP) and ammonium nitrogen ($NH_4^+−N$) were released during sludge fermentation (4). Thus, if the fermentation liquid were used as the additional carbon source of BNR, the following problems should be solved: how to conveniently separate the sludge to gain fermentation liquid as much as possible, and how to efficiently recover SOP and $NH_4^+−N$ to lower their potential loadings to the influent of BNR.

One commonly used technique for sludge−liquid separation is filtration. However, the deteriorated filtration capability of the fermented sludge made the conventional sludge dewatering method unpractical (5). Many methods such as freeze/thaw conditioning (7) and thermal conditioning (8) have been reported to improve sludge dewaterability. Nevertheless, these strategies are energy consuming and equipment eroding, which limit their applications.

As to the recovery of phosphorus or ammonium, although many strategies can be resorted, the method of struvite formation ($MgNH_4PO_4 \cdot 6H_2O$, MAP) has been a research focus in recent years because not only can SOP and $NH_4^+−N$ be simultaneously recovered, but also the formed struvite can be used as a slow-release fertilizer. Traditionally, MAP recovery was conducted after solids (sludge)−water (liquid) separation (Figure 1a) (4, 9). However, as mentioned above, it is hard to complete the sludge−liquid separation of fermented sludge. In order to improve the separation performance of sludge−liquid after WAS fermentation, and efficiently recover the released SOP and $NH_4^+−N$, we alternatively consider the feasibility of simultaneous SOP and $NH_4^+−N$ recovery in the formation of MAP before sludge filtration dewatering (Figure 1b). It was observed in our study that this alternative significantly improved the dewaterability of fermented WAS.

Thus, the main purpose of this study was to investigate the optimum conditions for simultaneous recovery of SOP and $NH_4^+−N$ from the fermented sludge−liquid mixture, and the effect of SOP and $NH_4^+−N$ recovery process on the filtration dewatering ability of the fermented sludge. Also, the mechanisms for simultaneous SOP and $NH_4^+−N$ recovery improving sludge dewaterability were investigated. Finally, the fermentation liquid was added to municipal wastewater to investigate its effect on biological nutrients removal performance.

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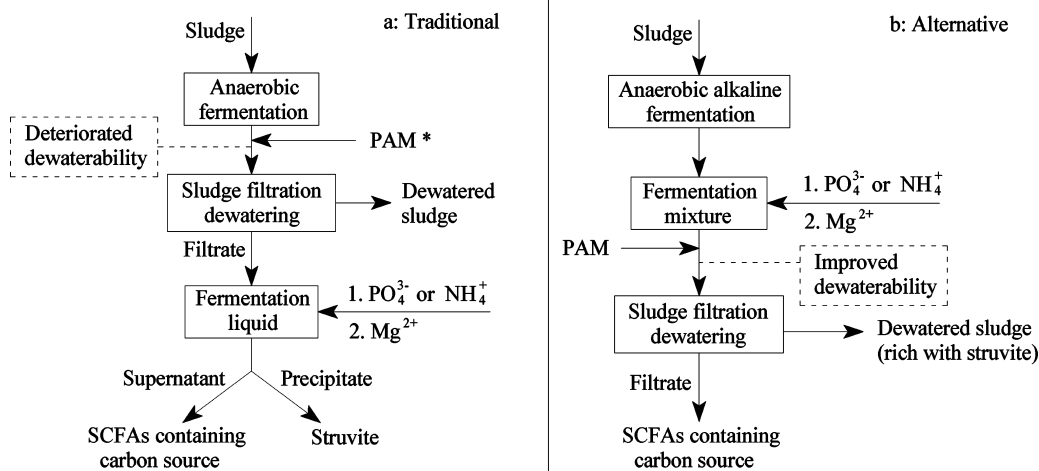
**FIGURE 1. Scheme of the traditional (a) and the alternative (b) process for SCFAs separation from fermented sludge (* even conditioned by polyacrylamide (PAM), the sludge dewaterability was still bad).**

**TABLE 1. Characteristics of the WAS before and after Alkaline Fermentation[a]**

|        | pH   | TSS (mg/L) | VSS (mg/L) | SVI (mL/g) | SRF (m/kg)           | CST (s) | MPS ($\mu$m) | $\zeta$ potential (mv) |
|--------|------|-----------|-----------|-----------|----------------------|---------|-----------|------------------------|
| before | 6.85 | 17331     | 12447     | 57.6      | $1.6 \times 10^{13}$ | 111     | 12.5      | −13.1                  |
| after  | 10.0 | 14298     | 8698      | 70.7      | $7.1 \times 10^{14}$ | >30000  | 3.1       | −20.9                  |

[a] TSS, total suspended solids; VSS, volatile suspended solids; SVI, sludge volume index; MPS, mean particle size.

## Materials and Methods

**Sludge and Its Alkaline Fermentation.** The WAS used for anaerobic alkaline fermentation was obtained from the secondary sedimentation tank of a WWTP in Shanghai, China, which was operated with a BNR process. The sludge was concentrated by settling at 4 °C for 24 h and then put into an anaerobic reactor with a working volume of 20 L for fermentation. The fermentation pH was controlled at 10.0 by adding 5 M NaOH solution, and the reactor was stirred at 100 rpm in a 21 ± 1 °C room for 8 days since the greatest production of total SCFAs achieved at this time (6). The sludge characteristics before and after fermentation are shown in Table 1. Obviously, the SRF and CST of the WAS after fermentation were much greater than that before fermentation, which indicated that the filtration dewaterability significantly deteriorated. After fermentation, the mixture (fermentation sludge and liquid) was collected for $NH_4^+$−N and SOP recovery and for filtration dewatering.

**Simultaneous $NH_4^+$−N and SOP Recovery Optimized by Response Surface Methodology.** When $NH_4^+$−N and SOP are simultaneously recovered in the formation of struvite from wastewater, parameters such as pH, Mg/N (mole ratio of $Mg^{2+}$/$NH_4^+$−N) and P/N (mole ratio of SOP/$NH_4^+$−N), have been reported to be the important variables (4, 10). Response surface methodology (RSM), a powerful tool for the evaluation of the interactive effects of multiple variables on process performance, was used to obtain the optimum $NH_4^+$−N and SOP recovery conditions in this study.

The experiments were carried out following a five-level-three-variable central composite design (CCD) composed of eight factorial points (coded as ±1), six axial points (coded as ±1.68), and six replications of center points (coded as 0), which was designed by Design Expert Software (version 7.0, Stat-Ease, Inc., U.S.). The repeated six central points were used to estimate the pure error of the experiment. The coded levels of the variables are shown in Table 2.

In the fermentation mixture, it was observed that the molar concentration of released $NH_4^+$−N (about 23 mmol/L) was greater than that of released SOP (about 8 mmol/L). In order to simultaneously recover the released $NH_4^+$−N and SOP in

**TABLE 2. Experimental Range and Coded Levels of the Independent Variables**

| coded levels | variable ranges | | |
|--------------|------|-------------|-------------|
|              | pH   | Mg/N (mol/mol) | P/N (mol/mol) |
| −1.68 | 9.16  | 1.23 | 0.8 |
| −1    | 9.50  | 1.50 | 1.0 |
| 0     | 10.00 | 1.90 | 1.3 |
| 1     | 10.50 | 2.30 | 1.6 |
| 1.68  | 10.84 | 2.57 | 1.8 |

the formation of struvite in which their theoretic molar ratio should be 1:1, $KH_2PO_4$ was added. Twenty batch experiments designed by CCD are illustrated in Table 3. For each test, 500 mL fermented mixture was put into a 1000 mL glass beaker and was mechanically stirred at 200 rpm. Then the pH was adjusted with 3 M NaOH or 3 M HCl as required, and a certain amount of $KH_2PO_4$ solution (140 g/L) and $MgCl_2 \cdot 6H_2O$ solution (320 g/L) were added. Distilled water was added to achieve an identical final volume of 520 mL in all tests. After reaction for 5 min, which was enough for struvite formation (Supporting Information (SI) Figure S1), the residual $NH_4^+$−N and SOP in the fermentation liquid were analyzed. The results are shown in Table 3.

According to the Design Expert software, each of the response (i.e., the residual $NH_4^+$−N or SOP) could be fitted by a predictive polynomial quadratic model (eq 1):

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j + \sum_{i=1}^{3} \beta_{ii} x_i^2 \quad (1)$$

where $Y$ represents the predicted residual $NH_4^+$−N or SOP concentration after struvite formation, $x_i$ and $x_j$ are the independent variables, and $\beta_0, \beta_i, \beta_j$ and $\beta_{ij}$ are the regression coefficients of the model.

After regression of the experimental data with eq 1, the interactive effects of the factors were analyzed on both surface plots and contour plots that derived from the Design Expert.

**TABLE 3. Experiments Designed by CCD and the Observed and the Predicted Responses**

| | coded levels | | | | response, Y | | | |
| | | | | | SOP (mg/L) | | NH$_4^+$−N (mg/L) | |
| run no. | x$_1$-pH | x$_2$-Mg/N | x$_3$-P/N | final pH | observed | predicted | observed | predicted |
|---|---|---|---|---|---|---|---|---|
| 1 | −1 | −1 | −1 | 8.66 | 38.49 | 42.89 | 76.56 | 75.80 |
| 2 | 1 | −1 | −1 | 10.04 | 19.95 | 23.74 | 94.59 | 97.06 |
| 3 | −1 | 1 | −1 | 8.51 | 32.63 | 37.87 | 73.20 | 75.42 |
| 4 | 1 | 1 | −1 | 9.87 | 8.72 | 8.86 | 103.44 | 100.72 |
| 5 | −1 | −1 | 1 | 8.30 | 196.35 | 197.81 | 39.15 | 43.21 |
| 6 | 1 | −1 | 1 | 9.97 | 82.33 | 78.69 | 36.55 | 35.67 |
| 7 | −1 | 1 | 1 | 7.98 | 148.99 | 146.81 | 29.06 | 27.92 |
| 8 | 1 | 1 | 1 | 9.74 | 20.62 | 17.83 | 22.32 | 24.42 |
| 9 | −1.68 | 0 | 0 | 7.72 | 150.49 | 145.96 | 72.94 | 70.98 |
| 10 | 1.68 | 0 | 0 | 10.20 | 19.14 | 21.40 | 85.85 | 85.92 |
| 11 | 0 | −1.68 | 0 | 9.56 | 78.68 | 75.88 | 42.26 | 40.00 |
| 12 | 0 | 1.68 | 0 | 9.20 | 19.95 | 20.48 | 29.84 | 30.21 |
| 13 | 0 | 0 | −1.68 | 9.51 | 6.52 | −0.78 | 107.79 | 107.71 |
| 14 | 0 | 0 | 1.68 | 9.18 | 132.01 | 137.03 | 17.96 | 16.15 |
| 15 | 0 | 0 | 0 | 9.31 | 19.33 | 22.93 | 30.90 | 33.25 |
| 16 | 0 | 0 | 0 | 9.33 | 27.37 | 22.93 | 35.90 | 33.25 |
| 17 | 0 | 0 | 0 | 9.38 | 24.51 | 22.93 | 35.34 | 33.25 |
| 18 | 0 | 0 | 0 | 9.34 | 26.81 | 22.93 | 33.49 | 33.25 |
| 19 | 0 | 0 | 0 | 9.36 | 19.54 | 22.93 | 32.33 | 33.25 |
| 20 | 0 | 0 | 0 | 9.35 | 20.62 | 22.93 | 31.22 | 33.25 |

By superimposing the contour plots on a contour plot, an overlay plot was produced in the software, and the optimum conditions for simultaneous NH$_4^+$−N and SOP recovery were obtained from the overlay plot.

**Sludge Dewatering Experiments.** First, 2500 mL of the fermented WAS was divided equally into five glass beakers and each was mechanically stirred at 200 rpm. Second, KH$_2$PO$_4$ solution (140 g/L) and MgCl$_2$·6H$_2$O solution (320 g/L) were added according to the optimum conditions determined above, and the mixture was stirred for 5 min for struvite formation. Third, cationic polyacrylamide (PAM) solution, and distilled water if necessary, were added into the sludge−liquid mixture to achieve a final volume of 600 mL in each beaker and stirred at 200 rpm for 2 min, and then changed to 20 rpm and stirred for 10 min. The stock concentration of PAM was 0.15% (w/w). The weight ratio of PAM to sludge was controlled at 0, 0.33, 0.67, 1.0, and 2.0%, respectively, in the five beakers to obtain the optimum PAM dosage. In order to study the sludge dewatering ability with no NH$_4^+$−N and SOP recovery, PAM was directly added into the fermentation mixture (500 mL) at PAM to sludge ratio of 0, 0.33, 0.67, 1.0, and 2.0%, respectively, and all the other operations were the same as those with NH$_4^+$−N and SOP recovery.

In order to investigate the effect of struvite on sludge dewaterability, standard struvite powder (purchased from Sigma) was added into 500 mL fermented mixture. The amount of the added struvite was the same as that theoretically produced in 500 mL fresh fermented mixture. Then PAM was added (PAM to sludge ratio was 1.0%), and the volume of the mixture was also adjusted to 600 mL by distilled water. The mixture was stirred in the same manner as mentioned above.

**Biological Nutrient Removal.** After the fermentation liquid was obtained according to Figure 1b under the optimum process conditions, it was used as the additional carbon source of municipal wastewater for BNR in a sequencing batch reactor (SBR). As a comparison, another SBR without fermentation liquid addition was run as a parallel control. The main characteristic of the municipal wastewater obtained from a WWTP in Shanghai was (mg/L) 180 COD, 4.9 SOP, 31 NH$_4^+$−N and 35 total nitrogen (TN). After fermentation liquid addition, the concentration of COD, SOP, NH$_4^+$−N, and TN in the wastewater was 350, 5.3, 31.5, and

36 mg/L, respectively. The SBRs, with a working volume of 3.5 L each, were operated on three 8 h (1.5 h anaerobic, 1 h aerobic, 1 h anoxic, 30 min aerobic, 1 h anoxic, and 20 min aerobic period, followed by 1 h settling, 5 min decanting and 95 min idle phase) cycles per day. The SBRs were maintained at 21 ± 1 °C, mixed with magnetic stirrers and controlled at a sludge retention time of approximately 20 days. The dissolved oxygen concentration was about 6 mg/L in the aerobic phase. After the settling period, 2.3 L supernatant was discharged, and replaced with 2.3 L fresh wastewater during the next initial 10 min of the anaerobic time. It was observed that the effluent nitrogen and phosphorus concentrations in two SBRs reached stable after culturing for around 70 days, and then the comparisons between two reactors were made.

**Analytical Methods.** The modified heat method was used for loosely bound extracelluar polymetric substances (LB-EPS) and tightly bound EPS (TB-EPS) extraction (11). SRF was performed according to Christensen and Dick (12) at a vacuum of 0.05 M Pa using Whatman No. 3 filter paper. Sludge capillary suction time (CST) was measured by CST instrument (model IFP-9050, Venture Innovations Ltd., U.S.) with Whatman No. 17 filter paper. The water percentage content (WPC) of filtrated sludge cake was measured according to Chen et al. (13). Concentrations of Mg$^{2+}$, Ca$^{2+}$, and K$^+$ were analyzed by inductively coupled plasma−optical emission spectrometer (ICP-OES, Optima 2100DV, PerkinElmer, U.S). $\zeta$ potential was measured on a Zetasizer (Nano-Z, Malvern Co. UK). Particle size was analyzed by Eyetech laser size analyzer (Ankersmid Ltd., Dutch). Ionic strength was calculated according to Ronteltap et al. (14).

Under the optimum NH$_4^+$−N and SOP recovery conditions, the WAS mixture was centrifuged at 8000 rpm for 10 min, and the centrifuged sludge cake was dried at 40 °C for 72 h to prevent the struvite crystals from losing their crystallization water (15), and then the dried sludge was examined by X-ray diffraction (XRD). XRD analysis of the dried sludge was carried out on D/max2550 VB3 system (Rigaku, Japan).

TN and total phosphorus (TP) were analyzed according to the standard method (16). The analyses of SCFAs (by gas chromatograph, HP5890), protein, polysaccharide, SOP, NH$_4^+$−N, soluble chemical oxygen demand (SCOD), TSS, and VSS were the same as described in our previous
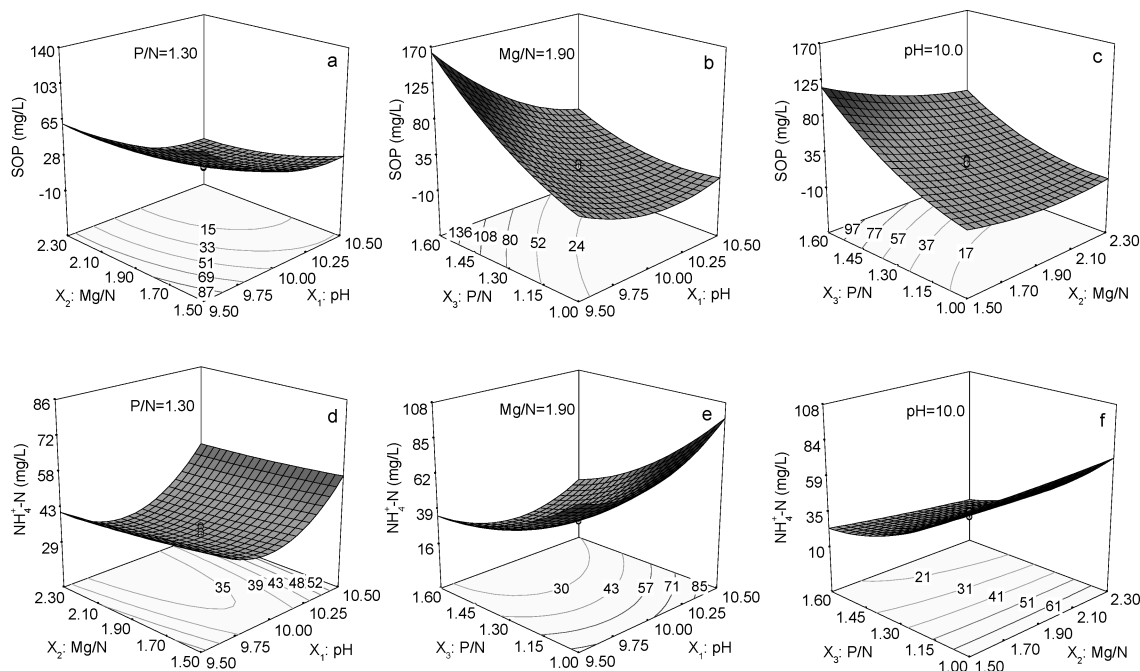
**FIGURE 2. Three dimensional surface plots and contour plots for SOP and $NH_4^+-N$ concentrations (a−c: effects of pH, Mg/N and P/N on SOP; d−f: effects of pH, Mg/N, and P/N on $NH_4^+-N$).**

publications (6, 13). The total SCFAs content was calculated as the sum of measured acetic, propionic, n-butyric, iso-butyric, n-valeric, and iso-valeric acid, and the total amount of EPS was recorded as the sum of measured protein and polysaccharide.

## Results and Discussion

**Response Analysis of SOP and $NH_4^+-N$ Recovery.** Although the run numbers of the experiments were sequentially listed in Table 3, the CCD tests were performed randomly to minimize the unpredicted environmental effects on the response. The observed data in Table 3 were first subjected to the regression analysis in Design Expert, and the fit summary suggested that the quadratic model was the most appropriate one among all of the polynomial models for the simulation of SOP or $NH_4^+-N$ concentration. The significance of the coefficients were determined and evaluated by analysis of variance (ANOVA). It should be noted that although the coefficients can be neglected if the corresponding P-value is larger than 0.05 (95% confidence) (SI Table S1), the insignificant terms were still reserved to maintain the integrity of the models. Consequently, the following mathematical regressions for the residual concentration of SOP and $NH_4^+-N$ were generated (in terms of coded factors):

$$Y_{SOP} = 22.928 - 37.032x_1 - 16.470x_2 + 40.972x_3 - 2.465x_1x_2 - 24.993x_1x_3 - 11.498x_2x_3 + 21.478x_1^2 + 8.927x_2^2 + 15.980x_3^2 \quad (2)$$

$$Y_{NH_4^+-N} = 33.251 + 4.440x_1 - 2.908x_2 - 27.223x_3 + 1.009x_1x_2 - 7.201x_1x_3 - 3.726x_2x_3 + 15.980x_1^2 + 0.656x_2^2 + 10.140x_3^2 \quad (3)$$

The second-order models were further justified by ANOVA (SI Table S2). The F-value of the models with a very low probability value (P-value less than 0.0001) demonstrates a high significance of the regression models. The values of the determination coefficient ($R^2$) were greater than 0.99 for both

$Y_{SOP}$ and $Y_{NH4-N}$, suggesting that the regression models were appropriate for simulating the experimental data, and less than 1% of the results could not be explained by the models. Also, both the values of the adjusted $R^2$ and the predicted $R^2$ were high enough to support the significance of the models. At the same time, the relative low values of the coefficient of variation (CV% = 9.37 for $Y_{SOP}$ and CV% = 5.36 for $Y_{NH4-N}$) indicated good precision and reliability of the models (17). The adequate precision, a parameter for the measurement of signal-noise with a desirable value of greater than 4, was also large enough for the models. Further details for the regression analysis are shown in SI Figures S2 and S3. Also, the predicted data were very close to the observed data (Table 3). Therefore, both of the models can be used for experimental prediction.

**Optimum Conditions for Simultaneous SOP and $NH_4^+-N$ Recovery.** Surface and contour plots of RSM as a function of two factors at a time, holding the third factor at a fixed level (normally at the zero level), are helpful in understanding the main and interaction effects of these two factors. As shown in Figure 2a, the increase of Mg/N ratio at a low pH level would not lead to obvious SOP reduction, while the increase of Mg/N at a high pH resulted in apparent SOP decrease. Figure 2b indicated that with the simultaneous increase in both P/N and pH, SOP recovery efficiency was enhanced. From Figure 2c, it can be seen that by increasing P/N and Mg/N at the same time, SOP recovery efficiency was also improved. In addition, pH appeared to be the critical factor that affected SOP concentration, since a slight rise in pH would cause a significant decrease in phosphorus content at a fixed ratio of either Mg/N or P/N.

The interactive effects of the variables on $NH_4^+-N$ are illustrated in Figure 2d−f. The interaction characteristic of Mg/N and pH appeared to be a U-shaped plot, which indicated that a moderate pH, such as pH 10, benefited $NH_4^+-N$ removal (Figure 2d). This conclusion was also supported by Figure 2e. Furthermore, Figure 2d and f suggested that $NH_4^+-N$ concentration was not significantly influenced by Mg/N ratio when both pH and P/N were controlled at constant levels.

In determination of the overlay plot, the maximum concentrations of the residual SOP and $NH_4^+-N$ after
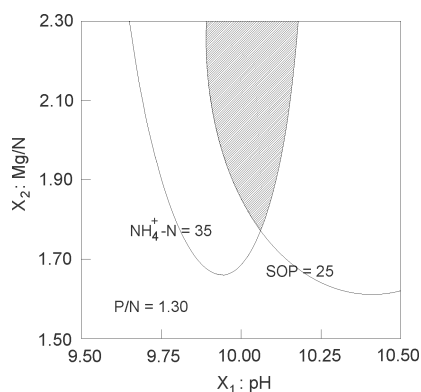
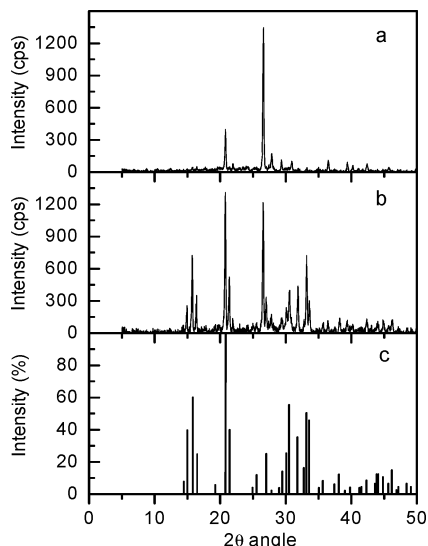**FIGURE 3. Overlay plot for optimum SOP and NH$_4^+$−N recovery (P/N = 1.30).**



**FIGURE 4. XRD diffraction pattern of the alkaline fermented sludge before (a) and after (b) SOP and NH$_4^+$−N recovery, and the diffraction pattern of standard struvite (c).**

recovery were set to be 25 and 35 mg/L, respectively, and the pH and Mg/N were set as the variable factors while P/N was set at different levels (SI Figure S4). It was observed that with P/N ratio increased from 1.30 to 1.60, the area of feasible response values (shadow area) inclined to move to the top right corner in the contour space (SI Figure S4), indicating that more Mg$^{2+}$ and alkali should be added with no obvious reduction of SOP and NH$_4^+$−N in the fermentation liquid. Thus, the optimum P/N ratio was determined as 1.30 in this study (Figure 3). As shown in the shadow area in Figure 3, the optimum Mg/N and pH for simultaneous SOP and NH$_4^+$−N recovery could be determined to be Mg/N = 1.9 and pH 10, which was at the center of the shadow zone. Under the optimum SOP and NH$_4^+$−N recovery conditions, the dried sludge was analyzed by XRD, which confirmed the presence of struvite (Figure 4).

The theoretical molar ratio of Mg:N:P in struvite should be 1: 1: 1, while the observed experimental molar ratio was 1.9: 1: 1.3 in this study. One reason for the Mg/N and Mg/P ratio being greater than 1:1 was that some soluble COD, such as protein, combined with Mg$^{2+}$ (4). In fact, most of the reported molar ratios in the literature were usually not in accordance with the theoretical ones. In the literature, the observed Mg/P was between 1.3 and 1.8 (4, 9, 18, 19), and P/N was between 1.1 and 1.67 (20−22). It seems that without sludge−liquid separation, the observed data in this study compared well with the reported ranges.

**Sludge Filtration Dewaterability.** It was observed that without NH$_4^+$−N and SOP recovery and with no PAM addition, the SRF and CST of the fermented sludge were 38.6 × 10$^{13}$ m/kg and 28 000 s, respectively. After filtration, the WPC of the fermented sludge was 97.2%. At PAM dosage of 1.0% without NH$_4^+$−N and SOP recovery, the SRF, WPC, and CST of the sludge were, respectively, 38.6 × 10$^{13}$ m/kg, 97.0% and 5532 s (Figure 5). At other PAM dosage, almost the same results were obtained (data not shown). Apparently, the fermented WAS was not suitable for filtration if merely conditioned by PAM.

With NH$_4^+$−N and SOP recovery, the filtration dewatering ability of the fermented WAS after PAM addition is shown in Figure 5. With the increase of PAM, the SRF, WPC and CST decreased, which reached the lowest (1.2 × 10$^{13}$ m/kg, 73.4% and 21 s, respectively) at PAM dosage of 1.0%, and further increasing PAM to 2% caused the increase of the SRF, WPC, and CST, indicating that the optimal PAM dosage was 1.0%. Obviously, the recovery of SOP and NH$_4^+$−N with the formation of struvite significantly improved the dewaterability of the fermented WAS, and after PAM conditioning, the SRF, CST, and sludge volume after filtration reduced to 3.1, 0.4, and 11.3%, respectively, of those without NH$_4^+$−N and SOP recovery at PAM dosage of 1.0%.

**Compositions of the Fermentation Liquor and the Sludge.** At fermentation time of 8 days, the main compositions of the fermentation liquid and the sludge after SOP and NH$_4^+$−N recovery and filtration dewatering are summarized in Table 4. For comparison, compositions of the fermentation liquid and the sludge of the fresh fermented mixture at 8 days are also included in Table 4.

It can be seen that about 90% SOP and NH$_4^+$−N were recovered from the fresh mixture, and partial SCOD, polysaccharide, and protein were also removed from the liquid. The SCFAs in the fresh and the filtrated fermentation liquid were 4276 and 4225 mg/L, respectively, indicating that SOP and NH$_4^+$−N recovery and PAM conditioning had little effect on the SCFAs concentration. The SCFAs in the filtrated fermentation liquid, which were composed of 31.0% acetic, 28.4% propionic, 17.6% iso-valeric, 11.5% iso-butyric, 8.6% n-butyric, and 2.9% n-valeric acid, accounted for 54.1% of the SCOD. Also, as seen in Table 4, TN, TP, Mg, and K in the filtrated sludge were, respectively, 1.83, 8.75, 203, and 1.67 times more than those in the fresh sludge, which indicated that the sludge fertility was significantly enhanced with the recovery of SOP and NH$_4^+$−N.

**Mechanisms of SOP and NH$_4^+$−N Recovery Improving Sludge Filtration Dewaterability.** As shown above, the filtration dewaterability of the fermented WAS with SOP and NH$_4^+$−N recovery was improved greatly compared to the sludge without SOP and NH$_4^+$−N recovery. In the literature, the ζ potential, polymeric substance (including solution biopolymers and EPS), and divalent cations have been reported to affect sludge dewatering, but very few studies discussed their influences on alkaline fermented sludge dewatering ability. A neutral potential is helpful in combining minor particles into big flocs because of the effect of precipitation-charge neutralization (23). It was observed that a clear breakpoint appeared in the ζ potential curve of the fermented sludge with SOP and NH$_4^+$−N recovery and 1.0% PAM dosage (SI Figure S5). At PAM dosage of 1.0%, the ζ potential was −19.4 mv with no SOP and NH$_4^+$−N recovery, whereas it was −10.3 mv with SOP and NH$_4^+$−N recovery (Table 5). Obviously, simultaneous recovery of SOP and NH$_4^+$−N neutralized the ζ potential.

As to the influence of polymeric substance, the content of solution biopolymers (protein and polysaccharide) decreased about 230 mg/L after SOP and NH$_4^+$−N recovery. On the other hand, the content of sludge LB−EPS with SOP and NH$_4^+$−N recovery decreased about 20% compared to
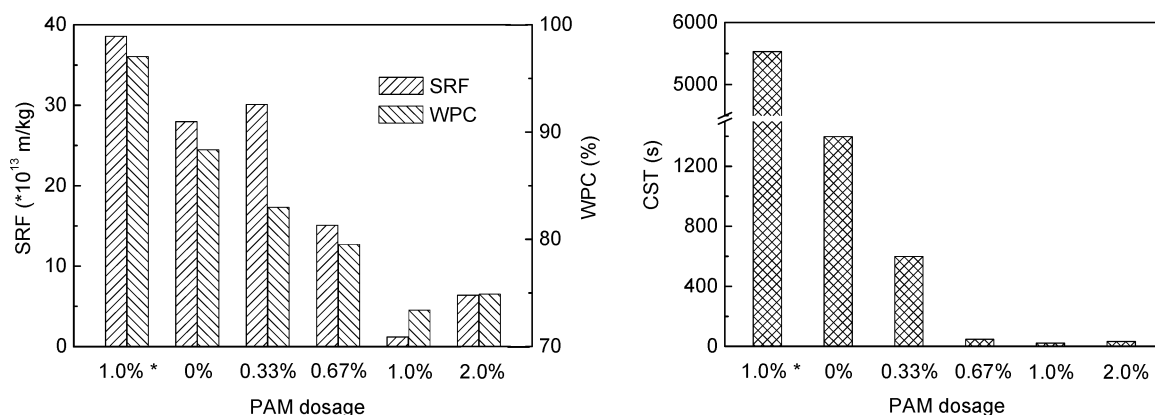
FIGURE 5. Effect of PAM dosage on dewatering ability of the fermented WAS after SOP and $NH_4^+$−N recovery (* dewatering ability of the fermented WAS without $NH_4^+$−N and SOP recovery at a PAM dosage of 1.0%).

**TABLE 4. Compositions of Fermentation Liquid and Dried Sludge before and after SOP and $NH_4^+$−N Recovery[a]**

| | fermentation liquid | | | | | | dried sludge | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SOP | $NH_4^+$−N | SCOD | SCFAs | polysaccharide | protein | TN | TP | Mg | K |
| fresh[b] | 213 | 275 | 8962 | 4276 | 222 | 1801 | 23 | 8 | 0.3 | 18 |
| filtrated | 18 | 27 | 8011 | 4225[c] | 161 | 1428 | 42 | 70 | 61 | 30 |
| removal efficiency | 91.5 | 90.2 | 10.4 | 1.2 | 27.5 | 20.7 | | | | |

[a] Units: SOP and $NH_4^+$−N, mg/L; SCOD, SCFAs, polysaccharide and protein, mg-COD/L; TN, TP, Mg, and K, mg/g-dried sludge; removal efficiency, %. [b] For direct comparison of the removal rate, 500 mL fresh fermented mixture was diluted to 600 mL with tap water. [c] SCFAs were composed of acetic 1309, propionic 1198, n-butyric 365, iso-butyric 487, n-valeric 123, and iso-valeric acid 742 mg of COD/L, respectively.

**TABLE 5. Comparison of $\zeta$ Potential and Polymer Substance with and without $NH_4^+$−N and SOP Recovery at PAM Dosage of 1.0%**

| | $\zeta$ potential (mv) | solution biopolymer (mg/L) | LB-EPS (mg/g-VSS) | $Mg^{2+}$ concentration (mmol/L) |
|---|---|---|---|---|
| with recovery | −10.3 | 1051 | 31.9 | 11.2 |
| without recovery | −19.4 | 1285 | 38.9 | 0.1 |

that without SOP and $NH_4^+$−N recovery (Table 5; TB−EPS was not included since it did not show obvious difference between the experiments). Clearly, both the solution biopolymers and sludge LB−EPS with SOP and $NH_4^+$−N recovery were lower than those without SOP and $NH_4^+$−N recovery. In the literature, the decrease of sludge biopolymers has been observed to be in consistent with the improvement of sludge dewaterability (5, 11, 13, 24).

As an integral part of sludge floc structure, divalent cations have also been reported to affect sludge filtration dewatering, and the increase of divalent cations can improve sludge dewaterabilty (5, 25). Due to the addition of $Mg^{2+}$ for simultaneous SOP and $NH_4^+$−N recovery, the measured $Mg^{2+}$ concentration after SOP and $NH_4^+$−N recovery was 11.2 mmol/L, which was 112 times of that without SOP and $NH_4^+$−N recovery (Table 5). Clearly, the SOP and $NH_4^+$−N recovery supplied large amount of $Mg^{2+}$, which benefited the formation of bigger flocs. The dewatering ability of the fermented sludge was therefore improved.

After SOP and $NH_4^+$−N recovery, the residual concentrations of SOP, $NH_4^+$−N, and $Mg^{2+}$ were 0.6, 2.0, and 11.2 mmol/L, respectively. Traditionally, it is thought that these ions can not coexist at such high concentrations at pH 9.35. It is therefore worthy to discuss the chemical equilibrium in our SOP and $NH_4^+$−N recovery system.

In water chemistry, the conditional solubility product ($P_s$), instead of solubility product constant ($K_{so}$), is often used to describe the equilibrium of struvite. $P_s$ is a function of pH and ionic strength ($\mu$), which has a value of $10^{-9.22}$ at pH 9.35 and $\mu = 0$ (26). The enhancement of $\mu$ will increase the value of $P_s$ and make the coexistence of high concentrations of SOP, $NH_4^+$−N and $Mg^{2+}$ possible. In this study, the value of $\mu$ was 0.16 due to the addition of NaOH (during WAS alkaline fermentation) and $MgCl_2$ and $KH_2PO_4$ (for simultaneous SOP and $NH_4^+$−N recovery). Thus, according to the literature (26), the theoretical $P_s$ was $10^{-7.8}$ at pH 9.35 and $\mu = 0.16$. In our experiments, the concentrations of $Mg^{2+}$, $NH_4^+$−N and SOP were 11.2, 2.0, and 0.6 mmol/L, respectively, at pH 9.35 after SOP and $NH_4^+$−N were recovered under the optimum conditions, and the calculated $P_s$ was $10^{-7.88}$, which was very close to the theoretical value ($10^{-7.8}$). Therefore, high concentration of $Mg^{2+}$ (11.2 mmol/L) could exist in our system.

During SOP and $NH_4^+$−N recovery, struvite was formed (Figure 4), which we think might affect sludge dewatering. After dosing commercial struvite into the fresh fermented sludge, it was observed that the SRF and CST was $21.1 \times 10^{13}$ m/kg and 1786 s, respectively, which decreased by 45.3 and 67.7%, respectively, compared to the sludge without struvite addition (Figure 5). It seems that the presence of struvite was also one reason for SOP and $NH_4^+$−N recovery improving fermented WAS filtration dewatering.

**Promoted BNR Performance.** In the control SBR, i.e., without fermented liquid addition, the effluent COD, TN, and SOP was 25, 13, and 2.6 mg/L, respectively, and the removal efficiencies of COD, TN and SOP were 86, 63, and 47%, respectively. To the SBR supplemented with fermentation liquid as the additional carbon source, the COD, TN and SOP were 31, 6, and 0.4 mg/L in the effluent, and the COD, TN, and SOP removal efficiency increased respectively to 91, 83, and 92%. It was obvious that both the nitrogen and phosphorus removals were enhanced by the addition of fermentation liquid.

## Acknowledgments

## Supporting Information Available

Tables S1 and S2 and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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