Optimization of Sludge Carbon Source Recovery from Waste Activated Sludge Thermo-alkaline Hydrolysis and Short-cut Fermentation Process

Junjie Li*, Ling Wang, Lina Pang

College of Architecture and Environment, Sichuan University, Chengdu 610065, China
122581115@qq.com

Organic products generated from waste activated sludge hydrolysis and fermentation process could be used as supplementary carbon source for enhanced biological nutrient removal. However, accompanied with organics production, large amount of ammonia nitrogen (NH4+-N) and soluble orthophosphorus (SOP) released, which would be negative to the reutilization of sludge carbon source. In this study, based on wasted activated sludge thermal-alkaline and short-cut fermentation process, optimal conditions for NH4+-N and SOP removal condition, and sludge carbon source recovery from short-cut fermentation liquid have been investigated systematically using response surface method. Results showed that, the removal rate of NH4+-N and SOP were 72.27% and 85.98% respectively, and the SCOD recovery rate was 80.74%.

1. Introduction

Along with a flourishing sewage treatment industry comes the pressing issues of urban sludge which is the byproduct of sewage treatment process, which generates excess activated sludge about 0.3-0.5% of the total sewage (assumed a moisture content at 97%). The cost for excess activated sludge treatment generally accounts for 25-65% of total operation cost of the sewage plant with large amount of energy and labor being consumed at the same time, and social and environmental problems are brought about from time to time. Studies show that the hydrolysis fermentation process of excess activated sludge can reduce the sludge quantity while generate a product which serves to enhance biological nutrient and reduce supplemented carbon source (Ji and Chen, 2010). Among many hydrolysis fermentation technologies, alkaline thermal hydrolysis of excess activated sludge can improve hydrolysis of particulate organic matter in the sludge in a short time and accelerate the recovering rate of sludge carbon source.

Apart from carbon source, byproducts like NH_4^+-N and soluble reactive phosphorus (SOP) are emitted during hydrolysis fermentation of sludge, and the emission amount of which usually leaves the microorganisms of traditional activated sludge system overburdened, especially the NH_4^+-N, which can inhibit nitrification (Anthonisen et al., 1976). Considering that phosphorus is a non-renewable and non-substitutable resource, a method or means which can remove nitrogen and phosphorus while recovering useful phosphorus is demanded for nitrogen and phosphorus removal process of fermentation broth. Studies reveal that the formation of $MgNH_4PO_4 \cdot 6H_2O$ (MAP) can reduce the nitrogen and phosphorus content in supernatant liquid of nitrifying sludge (Borgerding, 1972), so as to prevent overloading of nitrogen and phosphorus brought by sludge recirculation to sewage treatment. It can be concluded that the nitrogen and phosphorus removal method based on MAP can be used for nitrogen and phosphorus recovering during sludge anaerobic hydrolysis fermentation. Recent years see initial application of this method. Further, according to some studies, no absorption effect of dissolved organic matters was observed during the struvite precipitation process, which facilitates the recovering of sludge carbon source (Kelly and He, 2014).

Overseas and domestic scholars have contributed to thorough studies on MAP method in nitrogen and phosphorus removal (Lee et al., 2015, Çelen and Türker, 2001). Studies show that MAP method can remove nitrogen and phosphorus from hydrolytic acidification of excess activated sludge(Khan et al., 2016), however, there have not been any study on optimization of conditions for nitrogen and phosphorus removal from short-

range fermentation broth during sludge alkaline thermal hydrolysis, meanwhile, no particular and systematic study has been conducted towards sludge carbon source recovering during the optimization process.

2. Materials and Methods

2.1 Source of Excess Activated Sludge and Alkaline Thermal Hydrolysis Combined with Short-range Fermentation

The excess activated sludge used in the experiment was collected from the sedimentation tank of oxidation ditch of this lab and the sludge storage tank of local sewage plant. The excess activated sludge was sedimentated for 24h under 4 ^{o}C beforehand. Main indice of the excess activated sludge: total suspended solids (TSS) 9801±372 mg/L, volatile suspended solids (VSS) 6013±516 mg/L, total chemical oxygen demand (TCOD) 8308±156 mg/L, soluble chemical oxygen demand (SCOD) 98.2±7 mg/L, total polysaccharides (T-PS) 23.1±3 mgCOD/L, total protein (T-PN) 132.2±12 mgCOD/L, pH 6.5-7.2.

Based on early trials, setting for alkaline thermal hydrolysis combined with short-range fermentation was as follows: temperature of alkaline thermal hydrolysis 60 ^{o}C, pH12±0.2, and hydrolysis time 120 min. After alkaline thermal hydrolysis of sludge completed, the mixed liquor of above-mentioned sludge and alkaline was cooled to room temperature, with pH being adjusted to 9.0±0.2, and then transferred to the reactor inoculated with sludge for anaerobic hydrolysis fermentation, the proportion of which to the excess activated sludge was 0.4, the alkaline anaerobic fermentation was induced without temperature control. Concentration of initial excess activated sludge was controlled around 10gMLSS/L, the sludge was mixed using magnetic stirring apparatus (40-60 rpm), and alkaline thermal hydrolysis was carried out by heating the sludge in thermostat water bath. The fermentation lasted for 5 days. Parallel test was arranged for each group of experiment. Main ingredients of fermentation broth: NH_4^+-N 150±10 mg/L, SOP 170±10 mg/L, SCOD 2650±150 mg/L, pH 9.0±0.3.

2.2 Study on Nitrogen and Phosphorus Removal in Short-range Fermentation Broth

2.2.1 Experimental Method
According to informed researches, N/P mole ratio (recorded as N/P), Mg/N mole ratio (recorded as Mg/N), and pH were chosen as influencing factors in this study, the effects of the three factors exerted on the removal rates of NH_4^+-N, SOP and sludge carbon source (in terms of SCOD) at the time point of mixed for 3 min were evaluated, to conclude the optimal conditions for recovering nitrogen, phosphorus and sludge carbon source. During the optimization process, NH_4Cl and KH_2PO_4 were put into the supernatant liquid of the abovementioned fermentation broth to have N/P and Mg/N meet the experimental design requirements. The magnesium source adopted in this experiment was $MgCl_2 \cdot H_2O$, and mixing was conducted by magnetic stirring apparatus with digital display and temperature control.

2.2.2 Experimental Design of Response Surface Methodology
Response surface methodology is a technique combining mathematical statistics and experimental design, unlike orthogonal experimental method, the methodology is based on the interrelation between the influential factors and response values, by fitting to obtain an integrated regression model and expected levels of factors and response values, which makes the methodology more consummated in terms of experimental design and result interpretation.

In this study, the principle of circumscribed central composite design was adopted for experimental design, with X_1 (N/P), X_2 (Mg/N), and X_3 (pH) being chosen as independent variables, the removal rates (%) of NH_4^+-N, SOP, and SCOD as response values, the response surface analysis test with three factors and five levels was designed. The coded levels of experimental design were as shown in Table 1, in which, -1 represented the lowest level, 1 represented the highest level, α of distance from axial point to the center was set at 1.682.

Table 1: Independent factors and coded level based on circumscribed central composite design

Code	factor	unit	coded level				
			-1.682	-1	0	1	1.682
X_1	N/P	mol/mol	0.71	0.85	1.05	1.25	1.39
X_2	Mg/N	mol/mol	0.73	1.00	1.40	1.80	2.07
X_3	pH		8.66	9.00	9.50	10.00	10.34

The experiment results may be expressed in fitted cubic regression equation, as shown in Eq.1.

$$Y_{(1,2,3)} = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_i^2 + \beta_{ijk} X_i X_j X_k$$
$$+ \sum \beta_{iij} X_i^2 X_j + \sum \beta_{iii} X_i^3 \tag{1}$$

In which, $Y_{1,2,3}$ were expected response values (which were removal rates of NH_4^+-N, SOP, and carbon source in order), X_i, X_j, and X_k were independent factors (i=1-3; j=1-3; k=1-3; i, j, k were not equal to each other); β_0 was constant, β_i, β_{ij}, β_{ii}, β_{ijk}, β_{iij}, β_{iii} were regression coefficients, the fitting degree of polynomial model equation was indicated with R^2, the statistical significance of model equation was shown with P.

Design Expert 8.0（STAT-EASE Inc., Minneapolis, USA） was applied for experimental design, statistics analysis, and establishment of model for nitrogen and phosphorus treatment effects expectation.

3. Result and Analysis

3.1 Significance Testing of Prediction Model of Removal Rate

As per Design Expert analysis, the polynomial coding expression on removal rate models of $NH4^+$-N, SOP and SCOD was obtained as follows:

$$Y_1 = 63.71 + 4.07 X_1 + 7.49 X_2 + 4.46 X_3 - 8.78 X_1 X_2 + 3.24 X_1 X_3 + 1.85 X_2 X_3 - 0.03 X_1^2$$
$$-1.71 X_2^2 + 0.24 X_3^2 + 2.30 X_1 X_2 X_3 + 2.60 X_1^2 X_2 + 1.36 X_1^2 X_3 + 9.10 X_1 X_2^2 \tag{2}$$

$$Y_2 = 87.22 + 9.44 X_1 + 9.60 X_2 + 0.59 X_3 - 1.12 X_1 X_2 - 0.48 X_1 X_3 - 0.78 X_2 X_3 - 3.90 X_1^2$$
$$-9.96 X_2^2 - 0.29 X_3^2 - 0.01 X_1 X_2 X_3 - 9.48 X_1^2 X_2 + 2.65 X_1^2 X_3 + 3.95 X_1 X_2^2 \tag{3}$$

$$Y_3 = 19.58 + 1.10 X_1 + 0.34 X_2 - 0.86 X_3 + 1.67 X_1 X_2 + 0.01 X_1 X_3 - 0.08 X_2 X_3 + 0.71 X_1^2$$
$$+1.23 X_2^2 + 0.01 X_3^2 - 0.06 X_1 X_2 X_3 - 1.26 X_1^2 X_2 + 1.10 X_1^2 X_3 - 1.32 X_1 X_2^2 \tag{4}$$

The removal rate models of $NH4^+$-N, SOP and SCOD were analyzed by variance analysis through Design Expert software, so as to judge the rationality of the models.

3.1.1 Variance Analysis of Removal Rate Model of $NH4^+$-N
The variance analysis on the removal rate model of NH4+-N was shown in Table 2. In which, the F-value of model was 547.94, R2=0.9992, and the adjusted R2 (0.9973) was similar to the predicted R2 (0.9913), which indicated that the model and the experimental data shared relatively higher fitness; P value was less than 0.0001, which indicated that this model had higher significance, and can be used for predicting response value; F-value and P value of the model for lack of fit were 0.21 and 0.6656 respectively, which indicated that the lack of fit of model was not significant to pure error; the accuracy of model was 102.556 (>4), indicating that the model was reasonable. It showed that this item was significant when P<0.05, and the corresponding item was deemed as highly significant when P<0.01. Therefore, the information in Table 2 showed that $X1^2((N/P)^2)$ and X32(pH2) in the modeling expression had no significant impact to the removal rate of NH4+-N, but X12×X3((N/P)2×pH) had obvious significance to the model, other influencing factors had statistically significant influence towards the removal rate of $NH4^+$-N.

In conclusion, within the scope of three factors in this study, the removal rate model of NH4+-N established upon the experimental data was reasonable and effective, and it can be used for predicting the removal efficiency of NH4+-N in the forming process of struvite precipitation.

3.1.2 Variance Analysis of Removal Rate Model of SOP
The F-value of model was 283.30, R^2=0.9984, and the adjusted R^2(0.9948) was similar to the predicted R^2(0.8112), which indicated that the model and the experimental data shared relatively higher fitness; P value was less than 0.0001, which indicated that this model was highly significant, and it can be used for predicting response value; F-value and P value of the model for lack of fit were 5.49 and 0.0661 respectively, which indicated that the lack of fit of model was not significant to pure error; the accuracy of model was 55.501 (> 4), indicating that the model was reasonable. In the model expression, X_1(N/P), X_2(Mg/N), X_1^2((N/P)^2), X_2^2((Mg/N)^2) and $X_1^2 \times X_2$((N/P)^2×(Mg/N)) had statistically significant influence towards the removal rate of SOP, $X_1 \times X_2$((N/P)×(Mg/N)), $X_1^2 \times X_3$((N/P)^2×pH) and $X_1 \times X_2^2$ ((N/P)×(Mg/N)^2) had significant impact on the removal rate of SOP, other factors were not significant.

In conclusion, within the scope of all the factors in this study, the removal rate model of SOP established upon the experimental data was reasonable and effective, and it could be used for predicting the removal efficiency of SOP in struvite precipitation formation process.

Table 2: ANOVA for response surface model of NH4$^+$-N removal efficiency (*Significant; ** Very significant)

Source	Quadratic Sum	DOF	Mean Square	F-value	P-value	
Model	3813.28	13	293.33	547.94	<0.0001	**
X_1: N/P	93.72	1	93.72	175/04	<0.0001	**
X_2: Mg/N	317.55	1	317.55	593.18	<0.0001	**
X_3: pH	112.50	1	112.50	210.15	<0.0001	**
N/P×Mg/N	538.45	1	538.45	1005.82	<0.0001	**
N/P×pH	56.75	1	56.75	106.01	<0.0001	**
Mg/N×pH	27.44	1	27.44	51.25	0.0004	**
$(N/P)^2$	0.013	1	0.013	0.023	0.8834	
$(Mg/N)^2$	42.26	1	42.26	78.94	0.0001	**
$(pH)^2$	0.82	1	0.82	1.52	0.2630	
N/P×Mg/N×pH	23.85	1	23.85	44.55	0.0005	**
$(N/P)^2$×(Mg/N)	22.37	1	22.37	41.79	0.0007	**
$(N/P)^2$×pH	6.17	1	6.17	11.52	0.0146	*
(N/P)×$(Mg/N)^2$	310.41	1	310.41	579.85	<0.0001	**
(N/P)×pH^2	0.000	0				
$(Mg/N)^2$×pH	0.000	0				
(Mg/N)×pH^2	0.000	0				
$(N/P)^3$	0.000	0				
$(Mg/N)^3$	0.000	0				
pH^3	0.000	0				
Residual Error	5.03	6	0.54			
Loss of Quasi	1.95	1	0.13	0.21	0.6656	
Pure Error	3.08	5	0.62			
Overall Error	4032.79	19				

3.2 Optimization Analysis by Response Surface Methodology

In addition to using equation to describe models, in this study, the response surface drawing and/or contour chart were both used to more vividly and graphically describe the interaction relationship among the factors of the models, therefore, by analyzing and evaluating the interaction effect of all the influencing factors, the optimal conditions of process might be further determined. The contour line of response surface and the three-dimensional diagram of N/P, Mg/N and pH value upon taking the removal rates of NH$_4^+$-N, SOP and SCOD as the response values were respectively shown in Figure 1a, Figure 1b and Figure 1c.

The optimized result of response surface indicated that the removal rate of NH$_4^+$-N was reduced along with the increase of N/P and was increased along with the rising of Mg/N and pH value; the removal rate of SOP was increased along with the increase of N/P and Mg/N; the removal rate of SCOD didn't vary significantly with the N/P, but it was increased along with the increase of Mg/N, which might be caused by the fact that the magnesium ions could react with SCOD in the fermentation broth to a certain extent to form a precipitate [14]. In addition, the results also showed that the effect of pH value on the removal rates of SOP and SCOD was not significant. Upon investigating the three response values at the same time, it is concluded that the better technological conditions by using struvite process to recycle nitrogen and phosphorus were N/P=0.99, Mg/N=1.56, pH≈10.0. The better technological conditions by using struvite process to recycle nitrogen, phosphorus and sludge carbon source obtained in this study were different with those reported in the literature, mainly reflected in that the mole ratio of N/P and Mg/N required in this study was lower than those required in existing literature, which indicated that when the phosphate moles released from the sludge hydrolysis fermentation was less than NH$_4^+$-N, the phosphate content necessary for being replenished in this method was lower and the dosage of magnesium source was reduced accordingly. Besides, the optimization conditions obtained from this study also indicated to some extent that, compared with alkaline hydrolysis fermentation, the obtaining method of sludge carbon source based on short-range fermentation of alkaline

thermal hydrolysis could not only realize rapid release of ideal organic carbon source required by organisms in a short time, but also reduce the dosage of phosphorus which is non-renewable, during the recovery process of nitrogen, phosphorus and sludge carbon source.
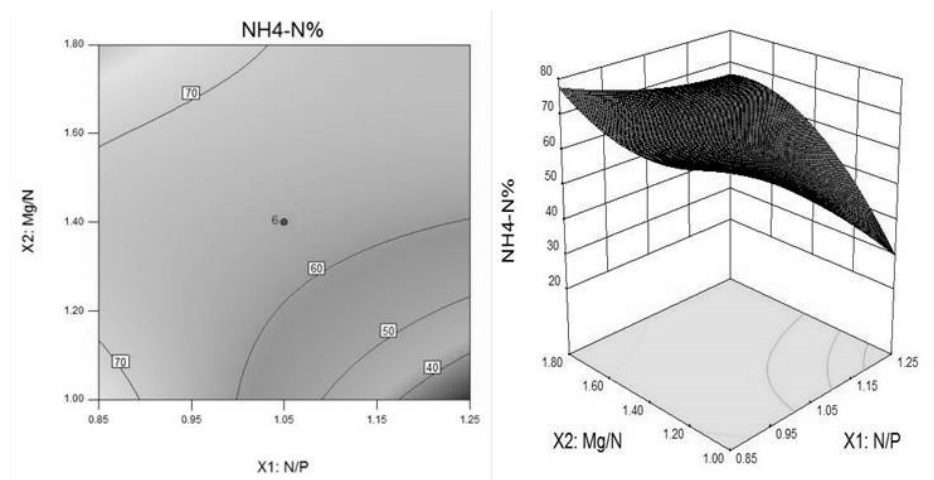
(a) The influence of N/P and Mg/N towards the removal rate of NH4+-N (pH=9.5)
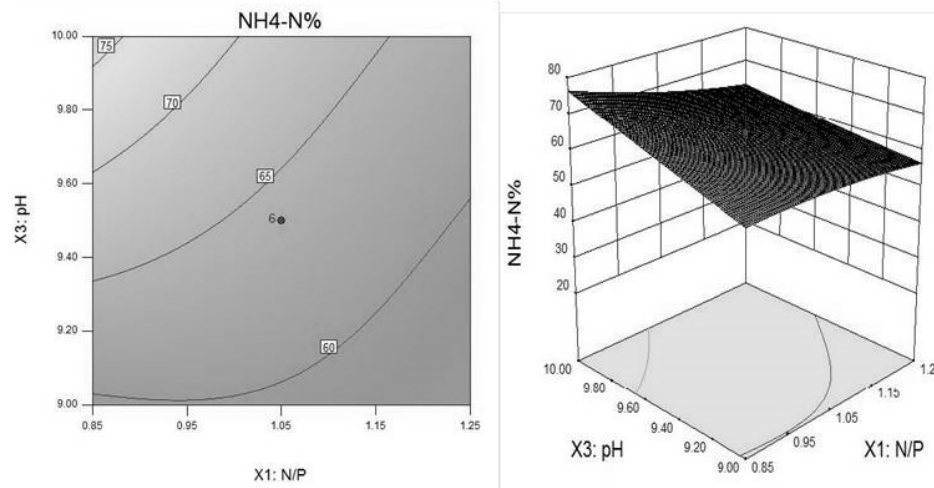
b) The influence of N/P and pH value towards the removal rate of NH4+-N (Mg/N=1.40)
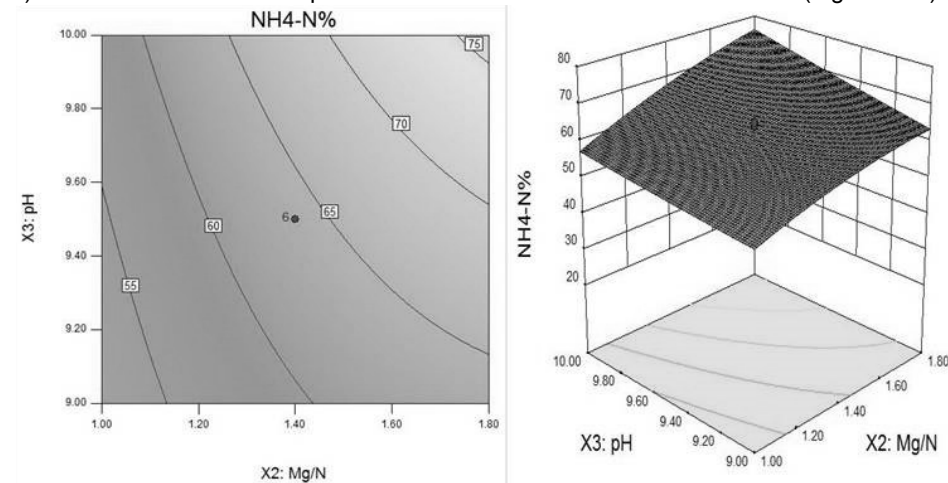
(c) The influence of Mg/N and pH value towards the removal rate of NH4+-N (N/P=1.05)

Figure 1: Three-dimensional response surface and contour diagrams of NH4+-N removal efficiency: (a) effect of N/P and Mg/N, pH=9.5; (b) N/P and pH, Mg/N=1.40; (c) Mg/N and pH, N/P=1.05.

4. Conclusions

The struvite precipitation was adopted in this study to optimize the recovery conditions of sludge carbon source under the best conditions of excess activated sludge alkaline thermal hydrolysis combined with short-range fermentation and the following conclusions of certain innovation were obtained:

(1) When removing the nitrogen and phosphorus from fermentation broth by using struvite, under the test conditions of pH8.5-10.5, N/P(mol/mol) 0.71-1.39, Mg/N (mol/mol) 0.73-2.07, the removal rate of NH_4^+-N was positively correlated with Mg/N and pH value respectively, but negatively correlated with N/P; the removal rate of SOP was positively correlated with N/P and Mg/N respectively, pH value had little effect on the removal rate of SOP; the removal rate of SCOD was not significantly affected by pH and N/P, but it was increased along with the increase of Mg/N.

(2) Through response surface analysis, the removal rate model (coding expression) of NH_4^+-N, SOP and SCOD within the interval of N/P(mol/mol)=0.71-1.39, Mg/N(mol/mol), pH 8.5-10.5 were established, upon verification, the removal rate model of NH_4^+-N, SOP and SCOD was deemed reasonable and reliable within the designed interval.

(3) Upon response surface analysis, under the best technological conditions of removal of nitrogen and phosphorus by using struvite, namely N/P=0.99, Mg/N=1.56, pH≈10.0 and stirring for 3 min., the removal rates of NH_4^+-N and SOP were 72. 27% and 85.98% respectively, the recovery rate of SCOD was 80.74% and the final pH value was about 9.52, the actual removal rate was quite close to the predicted value of model.

Reference

Anthonisen A.C., Loeher R.C., Prakasam T.B.S., Srinath E.G., 1976, Inhibition of Nitrification by Ammonia and Nitrous Acid, Water Pollution Control Federation, 48, 835.

Borgerding J., 1972, Phosphate Deposits in Digestion Systems. Journal, 44, 813-819.

Çelen I.T., Rker M., 2001, Recovery of Ammonia as Struvite from Anaerobic Digester Effluents. Environmental Technology, 22, 1263.

Dubois M., Gilles K., Hamilton J.K., Rebers P.A., Smith F., 1951, A colorimetric method forth determination of sugars. Nature, 168, 167.

Ji Z., Chen Y., 2010, Using sludge fermentation liquid to improve wastewater short-cut nitrification-denitrification and denitrifying phosphorus removal via nitrite. Environmental Science & Technology, 44, 8957.

Kelly P.T., He Z., 2014, Nutrients removal and recovery in bioelectrochemical systems: a review. Bioresource Technology, 153, 351.

Khan, A.A., Yudachev V., Lew B., 2016, Feasibility of phosphate precipitation from digested anaerobic sludge in a continuous aerated reactor. Desalination & Water Treatment, 1-6.

Lee E.Y., Min H.O., Yang S.H. Yoon T H., 2015, Struvite Crystallization of Anaerobic Digestive Fluid of Swine Manure Containing Highly Concentrated Nitrogen. Asian Australasian Journal of Animal Sciences, 28, 1053-1060.

Lowry O.H.N.G., ROSEBROUGH, N.J.J., Farr, A.L., Randall R.J.R., 1951, Protein Measurement With Folin Fenol Reagent. Journal of Biological Chemistry, 193, 265-275.