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Enhanced nitrogen and phosphorus removal in the A²/O process by hydrolysis and acidification of primary sludge

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ABSTRACT

Municipal wastewater treatment suffers the general problems of poor denitrification and low phosphorus removal caused by insufficient carbon sources. Thus, a baffled reactor was developed to provide additional carbon by hydrolysis and acidification of the primary sludge in the A^2/O process in order to treat low C/N ratio wastewater. The effects on denitrification and phosphorus removal were evaluated. The results showed that C_{TN}, C_{TP}, C_{COD}, and C_{NH⁴}-N in the effluent were concentrated at 17, 0.5, 30, and 1.6 mg/L, respectively, while the removal efficiencies rose to 69.6, 92.5, 88, and 96.7%, respectively, while dosing acidified primary sedimentation sludge. Compared with control groups that did not receive acidification liquid, C_{TN}, C_{TP}, and C_{NH⁴}-N of the effluent were decreased by 8.7, 1.3, and 0.7 mg/L, respectively, and the removal efficiencies were correspondingly increased by 15.6, 22.5, and 1.7%, respectively. These data demonstrated that adding acidified primary sludge effectively improved the removal of nitrogen and phosphorus nutrients.

Keywords: Primary sludge; Hydrolysis acidification; A²/O process; Denitrification and phosphorus removal

1. Introduction

Because organic content is insufficient in low C/N sewage, carbon sources fail to meet the requirements of denitrification, causing difficulties for the traditional biological denitrification process [1–4]. Thus, adding methanol, acetic acid, or other carbon sources (wheat straw, rice straw, or other cellulose) is recommended

when soluble chemical oxygen demand (SCOD) content is very low [5,6]. Recycling the sludge as a carbon source has been attracting wide attention because of the increasing difficulty of sludge disposal and the technological advances in the use of volatile fatty acid (VFA) extraction from sludge after hydrolytic acidification. Compared with external commercial carbon dosing, sludge recycling can make use of most carbon available in a wastewater treatment plant to supplement the influent SCOD, which has been considered

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one of the most suitable carbon sources for biological nutrient removal processes. This process is also sustainable and environmentally friendly. Some wastewater treatment plants have begun to use the method of hydrolytic acidification of excess sludge and primary sludge to supplement the influent carbon [7,8]. Recently, some Nordic countries such as Denmark and Sweden have successfully developed sidestream processes for the hydrolysis of activated sludge [9,10]. A great deal of research has been conducted in this field; for example, Gao et al. added excess sludge fermentation broth to the A^2/O system as the supplemental carbon source for biological nitrogen and phosphorus removal [11]; Lingqin Yu combined the A/O shortcut nitrification and denitrification process with the anaerobic hydrolysis of sludge, and added the sludge hydrolysis fermentation products to the anoxic zone of the A/O process as the carbon source for denitrification [12]. Primary sludge, which is rich in fatty acids with an organic matter content above 60%, is an ideal carbon resource [13-15]. Means of avoiding serious nitrogen and phosphorus release problems associated with the disposal of residual sludge has become an important field of research. In this study, primary sludge was chosen as the research object with a baffled reactor as the sludge fermentation unit for the hydrolytic fermentation of carbon sources. The baffled reactor had a continuous-flow configuration, composed of a multi-cell compartment. This arrangement has the advantages of both an upflow sludge bed reactor and a plug-flow reactor. The reactor volume was smaller than that of a CSTR reactor at the same substrate conversion rate, with a high transfer efficiency and without the need of stirring. The problem of a carbon source shortage can be better solved by making use of the organic carbon source in primary sludge by hydrolysis acidification, which combines sludge hydrolysis acidification with an improved biological treatment process, eventually realizing sludge resource use and stabilization.

2. Test device and method

2.1. Test device

The effective volume of the baffled reactor was 30 L. It was composed of four compartments, including two up-flow compartments and two down-flow compartments with a volume ratio of 1:4. The baffle plates were placed at a 45° angle to the bottom of the down-flow zone, and the effluent baffle in each compartment was 10 mm shorter than the prior one. The water bath surrounded the reactor peripherals, and

the temperature was thermostatically controlled at 30° C. The operating conditions were as follows: the volumetric load was 24 kg chemical oxygen demand (COD)/(m³ d), the hydraulic retention time (HRT) was 24 h, and the sludge retention time (SRT) was 3d. The reactor was made of plexiglass, and the test device configuration is shown in Fig. 1.

The A^2/O process is shown in Fig. 2 with the reactor's effective volume of 180 L, including the anaerobic tank, anoxic tank, and oxic tank with a volume ratio of 1:1:2. The effective volume of the secondary sedimentation tank was 40 L.

2.2. The quality of raw water

The raw water of A^2/O was sampled from a primary sedimentation tank effluent of a municipal sewage treatment plant of Beijing. The raw water quality is shown in Table 1. The C/N value of the sewage was 3.7-3.75, within the range of typical carbon-deficient wastewater. Electron donors from the substrate can only remove nitrogen or phosphorus individually rather than simultaneously.

The primary sludge was sampled from a primary sludge sedimentation tank of a municipal sewage treatment plant of Beijing. The pH value of the sludge was 6.8–7.5, the SCOD_{cr} was 300–350 mg/L, the VFA (acetic acid) concentration was 100–150 mg/L, TOC was 57–92 mg/L, carbonate alkalinity was 450–600 mg/L, TCOD_{cr} was 21.3–25.0 g/L, and NH₃-N was 84.9–95.6 mg/L.

2.3. Analysis method

The tested parameters and methods are shown in Table 2. The influent sludge was in a continuous-flow regime, in the test, and was taken from a primary sedimentation tank of a large urban sewage treatment plant.

3. Results and discussion

3.1. Nitrogen and phosphorus removal of the A^2/O process

In this test, the optimum operating conditions were set as follows: the water flow was 540 L/d, the water temperature was 20-25 °C, the sludge reflux ratio was 65-70%, the internal reflux ratio was 200%, the HRT was 8 h, the SRT was 13-14d, the dissolved oxygen of the aerobic stage was approximately 1.5-2 mg/L, and the sludge concentration of the aeration tank was 2,800-3,000 mg/L. As shown in Fig. 3, when the system was stable, the COD of effluent was approximately 25 mg/L and the NH⁴₄-N of effluent was less



Fig. 1. ABR primary sludge fermentation unit.



Fig. 2. Flow diagram of A^2/O process.

Table 1 Raw water quality (mg/L)

Parameter	Range
$C_{COD} \\ C_{NO_3^-} - N \\ C_{NH_4^+} - N \\ C_{TN} \\ C_{TP} $	200–210 0–0.5 43–45 54–56 6

than 2 mg/L. This means that the organic removal in the system was exceptional and the nitrifying bacteria performed well. However, the effluent TN was approximately 25 mg/L, which means the denitrification effect of the system was poor. In addition, the TP was 2 mg/L, indicating the dephosphorization effect of the system was poor, as well.

The nitrate in the return sludge increased the nitrate concentration of the inflow mixture. The nitrifying backflow increased the nitrate-nitrogen concentration and decreased the $C_{NH_4^+}$ -N of the anaerobic stage. The anaerobic stage did not perform well because of the sludge reflux of the A²/O process. The denitrifying bacteria utilized carbon resources, resulting in the nitrate-nitrogen of the inflow mixture being denitrified in the anaerobic stage, which was then carried back from the return sludge. The anaerobic stage was actually operated in an anoxic environment rather than an anaerobic environment until the nitrate-nitrogen was completely denitrified. This led to a release of a phosphorus-deficient material in the anaerobic stage, which weakened the subsequent

Table 2 Test items and methods

Parameter	Method	Parameter	Method
Chemical oxygen demand (COD _{Cr})	Potassium dichromate method	Ammonia nitrogen	Nessler's reagents spectrophotometer
TN	Persulfate oxidation—UV spectrophotometry	Nitrate-nitrogen	Thymol spectrophotometry method
pH values	Glass electrode method	SCOD	Spectrophotometry method
VFAs	Gas chromatography and five point pH method	Temperature	Water temperature meter method



Fig. 3. Characteristic diagram of A^2/O process before adding acidizing fluid.

absorption of phosphorus during the aerobic period. In the anoxic stage, the total phosphorus concentration decreased slightly, which may have been caused by the removal of denitrifying phosphorus [16].



Fig. 4. Effluent diagram of A^2/O process before adding acidizing fluid.

All the performance indicators for the effluent are shown in Fig. 4, when the A^2/O process ran at steady state. The average effluent COD was 25 mg/L, the average effluent NH_4^+ -N was 2.25 mg/L, the average TN was 25.7 mg/L, the average TP was 1.8 mg/L, and the removal efficiencies were 87.8, 95, 54, and 70%, respectively.

3.2. Efficiency of denitrification and phosphorus removal after dosing the acidification liquid

3.2.1. The quality of acidified liquid

In this test, the sludge acidizing fluid obtained from the baffled primary sludge acidizing technology was added in the A^2/O process to promote denitrification and phosphorus removal. When the baffled primary sludge hydrolytic acidification system was stable, the acidizing fluid water quality is shown in Table 3.

The dosing flow rate of sludge acidizing fluid was 18 L/d. After the sludge acidification liquid was dosed, the C_{COD} of the influent was 240–252 mg/L, $C_{\rm NH^+}$ -N was 45–48 mg/L, and $C_{\rm TP}$ was 6.5–6.9 mg/L.

3.2.2. Dosage of acidified liquid

The purpose of the baffled primary sludge acid hydrolysis process was to provide a ready source of biodegradable carbon for biological nitrogen and

Table 3 The acidizing fluid water quality (mg/L)

Parameter	Range
C _{SCOD}	1,500
C _{VFAs}	800
C _{NH⁺} -N	150
C_{TP}	15



Fig. 5. The acidizing fluid dosage effects on the TP and NH_4^+ -N of the effluent.

phosphorus removal, thus solving the problem of carbon deficiency in the influent wastewater. The SCOD concentration of the baffled primary sludge hydrolysis and acidification solution was approximately 1,500 mg/L, of which the VFA concentration was approximately 800 mg/L. The effective volume of the A^2/O reactor was 180 L. The effect that the acidified solution had on enhancing nitrogen and phosphorus removal was investigated when the dosage was 9, 18, 27, 36, and 45 L/d, respectively.

As shown in Figs. 5 and 6, the concentrations of TN, TP, and NH_4^+ -N in the A^2/O reactor effluent were significantly reduced because the acidified fluid carried some refractory organics which increased COD. When the dosage was 18 L/d, the effluent TN, TP, and NH⁺₄-N concentrations were 17.56, 0.42, and 1.48 mg/L, respectively. When the dosing was increased the TN, TP, and NH₄⁺-N concentrations ceased to decrease but instead showed a slight increase. These results showed that when the dosage of acidification liquid was 18 L/d, the VFAs could meet the requirement for the carbon source for nitrogen and phosphorus removal. With higher dosing, the effluent concentrations actually increased because of the nitrogen and phosphorus carried by the acidified fluid itself. Therefore, the appropriate dosage of acidified liquid was determined to be 18 L/d in the test.

3.2.3. Enhanced effect of nitrogen and phosphorus removal

After a certain period of cultivation and acclimation, the microbial populations in the A^2/O process achieved a new equilibrium and the process indicators gradually became stable. At this time, the reactor maintained an average sludge concentration of



Fig. 6. The acidizing fluid dosage effects on the COD and TN of the effluent.

approximately 3,500 mg/L. Fig. 7 shows the characteristic curve of enhanced nitrogen and phosphorus removal of the A²/O process after the system reached the new steady state with the acidified fluid dosage.

After dosing with the acidified fluid, the nitrogen and phosphorus in the sludge were also released in dissolved forms. Then, both carbon source and nitrogen and phosphorus content were increased in the influent of the A^2/O biological denitrification and dephosphorization process. The sludge acidification liquid provided a large amount of readily biodegradable organics and also carried nitrogen and phosphorus, increasing influent COD, $C_{NH_4^+}$ -N, and C_{TP} by 45, 3.0, and 0.8 mg/L, respectively.



Fig. 7. Characteristic diagram of the A^2/O process after adding acidizing fluid.

The C_{VFAs} of the carbon sources obtained by the hydrolytic acidification system accounted for approximately 50% of C_{SCOD}. The VFAs came from the readily biodegradable organics, providing sufficient electron donors for the oxidation-reduction reaction in the biological nutrient removal system [17]. When dosing with acidified fluid, the change of effluent quality of the nutrient removal process is as shown in Fig. 8. The results showed that adding the hydrolyzed primary sludge could improve the removal of nitrogen and phosphorus nutrients. The average TN value of effluent reached 17 mg/L, the average TP was 0.5 mg/L, the average COD was 30 mg/L, the average NH₄⁺-N was 1.6 mg/L, and the removal efficiencies were 69.6, 92.5, 88, and 96.7%, respectively. The effluent quality could meet the national water quality standard's A standards "Discharge standard of pollutants for municipal wastewater treatment plan" (GB 18918-2002).

3.3. Comparison of nitrogen and phosphorus removal before and after acidizing fluid dosing

The change in the quality of the effluent before and after dosing with the acidizing liquid is shown in Figs. 9 and 10. As shown in the figures, after dosing with acidizing fluid, the TN, NH_4^+ -N and TP all decreased but to a different extent. However, the COD illustrated an increasing trend. As shown in Fig. 9, the COD rose to 30 mg/L, indicating that a part of the refractory organics from the acidizing fluid were difficult to remove in conventional biological treatment systems.

After dosing with the acidified liquid, the TN, NH_4^+ -N, and TP were significantly reduced while the



Fig. 9. TN and NH_4^+ -N changes before and after adding acidizing fluid.



Fig. 10. COD and TP changes before and after adding acidizing fluid.



Fig. 8. Effluent diagram of A^2/O process after adding acidizing fluid.

	Before dosing the acidizing fluid		After dosing the acidizing fluid		Water quality changes	
Item	Average value (mg/L)	Average removal efficiency (%)	Average value (mg/L)	Average removal efficiency (%)	Reduction value (mg/L)	Increased removal (%)
TN	25.7	54.0	17.0	69.6	8.7	15.6
TP	1.8	70.0	0.5	92.5	1.3	22.5
COD	25.0	87.8	30.0	88.0	-5.0	0.2
NH ₄ ⁺ -N	2.3	95.0	1.6	96.7	0.7	1.7

 Table 4

 Effluent quality comparison before and after dosing with the acidizing fluid

Table 5 Comparison with similar processes

Technology	Improve TN removal (%)	Improve TP removal (%)
Methanol dosing technology	12.5	15.6
Adding acetic acid process	10.8	13.5
The process of excess sludge hydrolysis acidification	13.5	20.5
The technology of primary sludge hydrolysis acidification by vertical flow reactor	14.5	21.6

removal efficiencies increased correspondingly. This phenomenon can be explained as follows: the acidizing fluid provided an abundant carbon source for the A^2/O process. After dosing with acidizing fluid, the nitrate which was carried back through the reflux sludge to the anaerobic stage used the high quality carbon source as an electron donor, which can remove nitrate ions quickly, and eliminate the anoxic environment. This flow into the anaerobic zone changed to the anaerobic state quickly, providing conditions for polyphosphate accumulation organisms (PAO) to fully release phosphorus. In the anoxic section, the nitratenitrogen of the digester fluid backflow was removed by denitrification in the presence of an excess carbon. As it entered the oxic section, NH₄⁺-N was oxidized into nitrate-nitrogen by nitrifying bacteria. This was the main source of effluent nitrate-nitrogen. Because PAO fully released phosphorus and synthesized PHB in the anaerobic section, and then fully accumulated phosphorus in the oxic section, C_{TP} of effluent decreased to approximately 0.5 mg/L.

Table 4 compares the changes of water quality and the removal efficiency before and after dosing acidified fluid.

3.4. Comparison with similar processes

As shown in Table 5, the TN and TP average removal efficiencies were up to 69.6 and 92.5%, which was an increase of 15.6 and 22.5%, respectively, com-

pared with those without adding the acidified liquid. Many scholars, in China and internationally, had conducted research on enhancing nitrogen and phosphorus removal by developing alternative carbon sources [18–21]. Table 5 shows the effects on nitrogen and phosphorus removal by different carbon sources. As shown in the table, the baffled primary sludge hydrolytic acidification reactor was most effective for TN and TP removal.

4. Conclusions

- (1) Before dosing with the acidizing fluid, the average COD of the effluent was 25 mg/L, the average NH₄⁺-N of the effluent was 2.25 mg/L, the average TN of the effluent was 25.7 mg/L, the average TP of the effluent was 1.8 mg/L, and the removal efficiencies for these species were 87.8, 95, 54, and 70%, respectively. The results showed that the organic matter removal was effective, denitrifying bacteria nitrification was improved, but the denitrification and phosphorus removal effects were relatively small.
- (2) After dosing with acidified primary sedimentation sludge (18 L/d), the effluent C_{TN} was 17 mg/L, effluent C_{TP} was 0.5 mg/L, effluent C_{COD} was 30 mg/L, effluent $C_{NH_4^+}$ -N was 1.6 mg/L, and removal efficiencies for these species were up to 69.6, 92.5, 88, and 96.7%,

respectively. Compared with those without dosing with acidification liquid, the C_{TN} , C_{TP} , and $C_{NH_4^+}$ -N in the effluent were reduced by 8.7, 1.3, and 0.7 mg/L, respectively; and the removal was increased by 15.6, 22.5, and 1.7%, respectively. The results showed that adding primary sludge acidizing fluid improved the effective removal of nitrogen and phosphorus nutrients.

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References

- [1] L. Carrio, F. Streett, K. Mahoney, C. deBarbadillo, J. Anderson, K. Abraham, N. Passarelli, Practical considerations for design of a step-feed biological nutrient removal system, Proc. Water Environ. Fed. 2000(11) (2000) 803–823.
- [2] J. Li, J. Ren, X. Yang, W. Ma, J. He, T. Li, The chemical-aid phosphorus removal from municipal wastewater with limited carbon source, J. Beijing Univ. Technol. 35(10) (2009) 1396–1401.
- [3] W. Liu, J. Li, W. Song, W. Ma, X. Yang, J. He, T. Li, Influence of carbon source on nitrogen and phosphorus removal by anoxic/anaerobic/aerobic process, Chin. Water Wastewater 25(13) (2009) 55–57.
- [4] S. Xia, L. Jiang, H. Wang, Z. Zhang, Enhanced biological phosphorus removal in a novel sequencing membrane bioreactor with gravitational filtration (GFS-MBR), Desalin. Water Treat. 9 (2009) 259–262.
- [5] J. Liu, Z. Luo, M. Jin, J. Lian, Y. Li, Wheat straw as carbon sources of aerobic denitrification, Environ. Eng. 26(2) (2008) 94–96.
- [6] L. Shao, Z. Xu, W. Jin, H. Yin, B. Zhu, Nitrate removal from wastewater using rice straw as carbon source and biofilm carrier, Environ. Sci. 30(5) (2009) 1414–1419.
- [7] P. Llabres, P. Pavan, P. Battistioni, F. Cecchi, J. Mata-Alvarez, The use of organic fraction of municipal solid waste hydrolysis products for biological nutrient removal in wastewater treatment plants, Water Res. 33 (1) (1999) 214–222.

- [8] J. Duan, W. Li, K. Zhao, J. Krampe, Variation of organics, nitrogen and phosphorus within a cycle of a biodenipho system, Desalin. Water Treat. 40 (2012) 24–32.
- [9] K. Andreasen, G. Petersen, H. Thomsen, R. Strube, Reduction of nutrient emission by sludge hydrolysis, Water Sci. Technol. 35(10) (1997) 79–85.
- [10] Z. Liu, C. Hu, W. Zhan, M. Liu, J. Yang, Side-strewn sludge bio-augmentation technologies and their applicability in upgrading and reconstruction of wastewater treatment plants, Chin. Water Wastewater 26(16) (2010) 1–6.
- [11] Y. Gao, Y. Peng, J. Zhang, S. Wang, J. Guo, L. Ye, Biological sludge reduction and enhanced nutrient removal in a pilot-scale system with 2-step sludge alkaline fermentation and A²O process, Bioresour. Technol. 102(5) (2011) 4091–4097.
- [12] L. Yu, Study on nitrogen removal performance of shortcut nitrification–denitrification in A/O coupled with sludge hydrolysis, Dalian University Technology, 2009.
- [13] R. Roxburgh, R. Sieger, B. Johnson, B. Rabinowitz, S. Goodwin, G. Crawford, G. Daigger, Sludge minimization technologies-doing more to get less, Proc. Water Environ. Fed. 2006(13) (2006) 506–525.
- [14] J. Ma, Y. Zhao, H. Zhang, Y. Wei, D. Niu, X. Chai, Research on methods of sludge disposal by landfill for urban wastewater treatment plants, Water Wastewater 33(10) (2007) 50–53.
- [15] S. Okabe, Y. Oozawa, K. Hirata, Y. Watanabe, Relationship between population dynamics of nitrifiers in biofilms and reactor performance at various C:N ratios, Water Res. 30(7) (1996) 1563–1572.
- [16] W. Ng, S. Ong, J. Hu, Denitrifying phosphorus removal by anaerobic/anoxic sequencing batch reactor, Water Sci. Technol. 43(3) (2001) 139–146.
- [17] B. Abbassi, S. Dullstein, N. Räbiger, Minimization of excess sludge production by increase of oxygen concentration in activated sludge flocs; experimental and theoretical approach, Water Res. 34(1) (2000) 139–146.
- [18] J. Lv, Y. Zhao, J. Wang, J. Zhou, H. Wang, C. Zhang, L. Zhang, Effects of primary sludge hydrolysis on enhanced biological phosphorous removal in A²/O process, J. Beijing Univ. Technol. 34(9) (2008) 981–985.
- [19] Y. Gao, Y. Peng, S. Wang, Using sludge hydrolysisacidification liquor as carbon source for nitrogen and phosphorus removal in A²/O Systan, Chin. Water Wastewater. 25(17) (2009) 23–27.
- [20] P. Li, X. Zheng, Y. Sun, Q. Wei, M. Yang, K. Sui, J. Li, Y. Chen, Pilot-scale study on efficient primary sedimentation tank with fermentation for treatment of municipal sewage, Chin. Water Wastewater 28(5) (2012) 5–8.
- [21] J. Cao, L. Hou, F. Fang, X. Jiang, M. Xiao, X. Chen, Effect of temperature and external carbon source on simultaneous nitrogen and phosphorus removal, Chin. J. Environ. Eng. 7(6) (2013) 2013–2018.