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Activated sludge ozonation to reduce sludge production in membrane bioreactor (MBR)

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Abstract

Total experimental period was divided into two stages. At first stage, a series of batch studies were carried out to get an understanding of the effect of ozonation on sludge properties. At the following stages, three membrane bioreactors (MBRs) with different amounts of activated sludge to be ozonated were run in parallel for a long period to evaluate the influence of sludge ozonation on sludge yield and permeate quality. Through batch study, it was found that ozone could disrupt the cell walls and cause the release of plasm from the cells, then the amounts of soluble organics in the solution increased with ozonation time. With the rise of soluble organics, the amount of soluble organics to be mineralized increased as well, which would reduce the soluble organics content. For the counteraction between these two aspects, a pseudo-balance could be achieved, and soluble organics would vary in a limited range. Sludge ozonation also increased the contents of soluble nitrogen and phosphorus in the solution. On the basis of batch study, a suitable ozone dosage of 0.16 kg O_3/kg MLSS was determined. Three systems were run in parallel for a total period of 120 days; it was demonstrated that a part of activated sludge ozonation could reduce sludge production significantly, and biological performance of mineralization and nitrification would not be inhibited due to sludge ozonation. Experimental results proved that the combination of ozonation unit with MBR unit could achieve an excellent quality of permeate as well as a small quantity of sludge production, and economic analysis indicated that an additional ozonation operating cost for treatment of both wastewater and sludge was only 0.096 Yuan (US$ 0.0115)/m^3 wastewater.

Keywords: Ozonation; Membrane bioreactor (MBR); Sludge production; Permeate quality

1. Introduction

The activated sludge treatment of wastewater results in the generation of a considerable amount of activated sludge that has to be wasted. Many treatments such as dewatering, digestion, burning, landfilling and use in agriculture have been carried out for the disposal of excess sludge. Because these treatments cost a great deal, an increasing interest exists in the reduction in the amount of sludge produced in the wastewater treatment process. Previous laboratory studies have demonstrated that the net biomass growth could be reduced under cryptic conditions [1–4]. Research shows that microbial cell lysis can be amplified by prolongation of sludge retention time (SRT) or through physicochemical treatments of sludge, such as thermal, alkaline or acid [5–7]. Based on these findings, it is hypothesized that cryptic growth phenomenon may be a feasible approach to achieve the goal of reducing sludge production.

Membrane bioreactor (MBR), a combination of a biological reactor with membrane separation technique, presents advantage of a complete dissociation and control of the hydraulic and biomass retention times. All sludge can be kept in MBR and SRT should be long enough. Material balance on COD in MBR shows that around 90% of the influent COD is oxidized to carbon dioxide and suspended solid concentration in the reactor is almost constant without sludge wastage [6].

Ozone is a very reactive oxidizing agent; it reacts with sludge compounds in two different ways, the direct and the indirect reaction [8]. Both reactions occur simultaneously; the direct reaction rate is lower and depends on the structure of the reactants. In this study, ozone was used as an oxidant to induce the death and lysis of biomass, and to improve the biodegradability of the dead biomass, then the ozonated sludge was recycled

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into MBR as substrate for further metabolism. The aim of the research is to reduce sludge production by the addition of activated sludge ozonation into MBR.

2. Materials and methods

A hollow fiber polyethylene ultra-filtration (UF) membrane unit with a total surface area of 2.0 m^2, mean pore size of 0.05 μm and a length of 0.35 m was used as the test membrane. The volume of the aerobic reactor was 16.3 L, and the temperature of the mixed liquid was maintained at 20 °C with a thermostat. The air was fed into the reactor with a micro-bubble air diffuser, and air flow rate was adjusted by an air flow-meter. There were all three systems of MBR, in which the HRT and DO were kept at 6 h and 2 mg L^{-1}, respectively. In addition, ozonation of the activated sludge was carried out in a contact column with an inner diameter of 5 cm and a height of 1.0 m. Ozone was introduced into the column through a diffuser located at the bottom of the column, and the ozonated sludge was recycled into MBR through a pump. A schematic diagram of the process configuration is shown in Fig. 1.

A synthetic domestic wastewater was used in this test study, which was prepared by mixing tap water with certain quantities of starch, sugar, NH_4Cl, Na_2HPO_4, NaH_2PO_4, $NaHCO_3$ and Na_2CO_3, and its characteristics are summarized in Table 1.

All analytical items were measured according to the Standard Methods [9].

Total experimental period was divided into two stages. At first stage, a series of batch tests were conducted to investigate the influence of ozonation on activated sludge, and the aim was to obtain a suitable ozone dosage. Then three MBRs with different amounts of activated sludge to be ozonated were run in parallel for a long period to evaluate the influence of sludge ozonation on sludge yield and permeate quality.

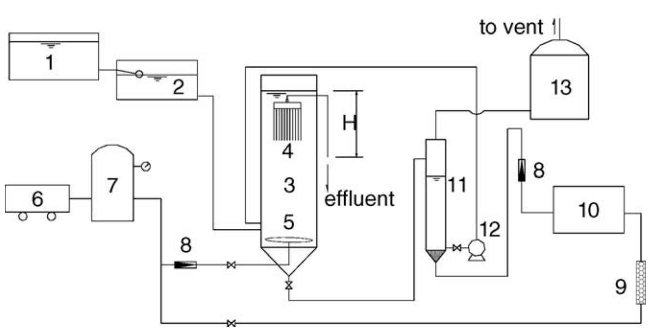

Fig. 1. Schematic of the experimental system: (1) storage tank; (2) constant high level tank; (3) aerobic reactor; (4) membrane module; (5) air diffuser (6) air compressor; (7) pressurized air storage vessel; (8) air flow-meter; (9) air drier; (10) ozone generator; (11) ozone contact column for sludge; (12) ozonated sludge recycle pump; (13) collecting device for ozone off-gas.

Table 1
The characteristics of the test wastewater

Parameter	Range	Mean
pH	6.92–7.86	7.16
SS (mg L^{-1})	112–252	178
COD (mg L^{-1})	215–420	342
NH_3-N (mg L^{-1})	24–54	41
TN (mg L^{-1})	34–68	54
TP (mg L^{-1})	2.4–5.1	3.2

3. Results and discussion

3.1. Batch study (first stage)

One set of experiment was performed to investigate the variation of SCOD of the sludge samples with ozonation. Activated sludge discharged from the reactor was split equally into two parts. One sample was filtered by qualitative filter paper with pore size of 0.45 μm and the filtrate was ozonated, whereas the other sludge sample was directly ozonated without filtering. Both sludge samples were ozonated at the same ozone dosage for 1 h. SCOD of the samples were determined at the beginning and at the end of the experiments.

Ozonation of the samples was conducted in a bubble column with an inner diameter of 80 mm and a height of 1.0 m, and ozone laden air stream was introduced into the column through a diffuser located at the bottom of the column.

The operation conditions were as follows: MLSS 5260 mg L^{-1}; air flow rate 200 L h^{-1}; ozone concentration 1.2 mg L^{-1}. The result of ozonation test is shown in Fig. 2.

As can be seen from Fig. 2, SCOD of the filtered solution had a slight decrease with ozonation, which should be ascribed to the direct ozonation for soluble organics, whereas SCOD of unfiltered liquid with activated sludge in it had a significant increase. Therefore, it was concluded that ozonation results in cell lysis and the increase in SCOD was mainly due to cell lysis.

On this basis, another batch test was carried out to investigate the influence of ozonation on sludge properties. Three liters of activated sludge was filled into the bubble column, and time series samples were taken for measurement of SCOD, BOD, MLSS, MLVSS, NH_3-N, NO_2^--N, NO_3^--N, TN, PO_4^{3-}-P and TP through the course of the test.

3.1.1. Effect of ozonation on SCOD and BOD

SCOD increased from 30 mg L^{-1} to 185 mg L^{-1} at the initial 2 h of ozonation, and decreased at a slow rate to 160 mg L^{-1} at the following 2 h. BOD reached its maximum value of 52 mg L^{-1} from initial 6 mg L^{-1} and was kept in a limited range of 30–40 mg L^{-1}. BOD/SCOD increased from 0.20 to 0.43 after

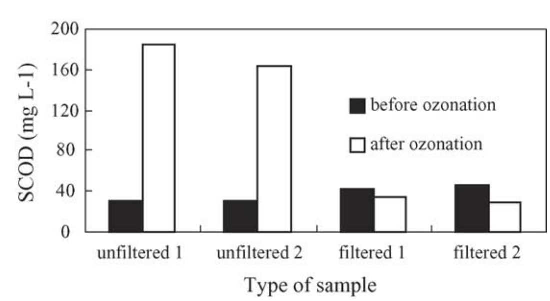

Fig. 2. Variation of SCOD of filtered and unfiltered sludge sample before and after ozonation.

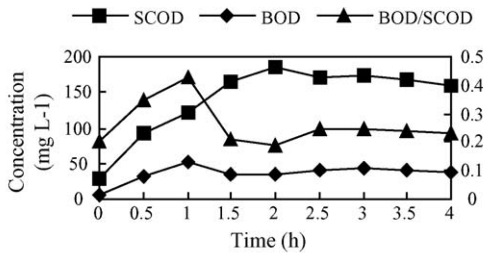

Fig. 3. Variation of SCOD, BOD and BOD/SCOD with ozonation time.

1 h of ozonation and thereafter decreased to around 0.2. According to the test result shown in Fig. 3, it was analyzed that there was a low content of soluble organics in the mixed liquid, and the amount of organics was oxidized directly by ozone was negligible, which could be deduced from the above test data. Therefore, the majority of ozone could disrupt the cell walls and caused the release of organic substrate from the cells, then the SCOD and BOD would rise with the increase of soluble organics in solution. With the increase of soluble organics, the amount of soluble organics to be mineralized increased as well, which would reduce the soluble organics content. On the one hand, sludge ozonation increased the amount of soluble organics; on the other hand, the increase of SCOD supplied more chances for the reaction between ozone and soluble organics and caused an increasing reduction in SCOD. For the counteraction between these two reactions, a pseudo-balance could be achieved, and the SCOD would vary in a limited range. As to the variation of BOD, it was concluded that a part of organics released from cell walls was biodegradable, which resulted in the rise of BOD at the initial 1 h of ozonation, and BOD/SCOD increased as well. At the following 0.5 h of ozonation, a part of BOD was mineralized causing a reduction in BOD, whereas SCOD increased in this period. Therefore, BOD/COD decreased from 0.43 to 0.21. During the ozonation period of 2–4 h, the amount of BOD contained at soluble organics released from the cells corresponded to that of being mineralized and BOD was kept relatively stable.

3.1.2. *Effect of ozonation on MLSS and MLVSS*

It can be seen from Fig. 4 that MLSS and MLVSS were always decreasing during 4 h of ozonation, and MLVSS/MLSS decreased from initial 0.90 to final 0.74. By analysis of test data, it can be deduced that the decrease of MLSS was mainly due to the decrease of MLVSS, because the decreased MLVSS accounted for main part of the lost MLSS, and MLVSS was a

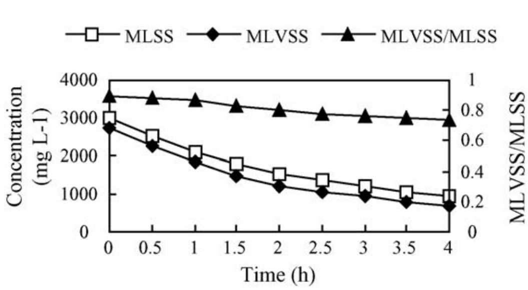

Fig. 4. Variation of MLSS, MLVSS and MLVSS/MLSS with ozonation time.

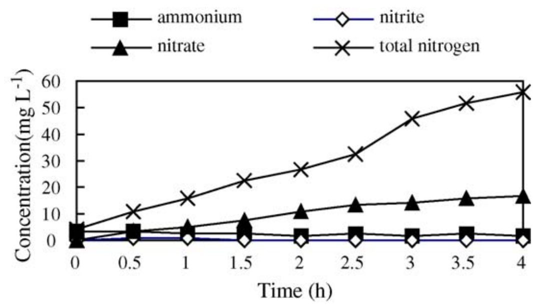

Fig. 5. Variation of NH_3-N, NO_2-N, NO_3^--N and TN with ozonation time.

part of MLSS. Therefore, the ratio of MLVSS/MLSS reduced with the prolongation of ozonation time.

3.1.3. *Effect of ozonation on NH_3-N, NO_2^--N, NO_3^--N and TN*

The NH_3-N, NO_2^--N, NO_3^--N and TN in solution were also detected, and the result is depicted in Fig. 5. During the course of ozonation, variation of NH_3-N and NO_2^--N was very limited, whereas there was a significant rise in NO_3^--N and TN. During 4 h of ozonation, NO_3^--N increased from 0.3 mg L^{-1} to 17.1 mg L^{-1}, and TN increased from 4.0 mg L^{-1} to 55.9 mg L^{-1}. Therefore, the organic nitrogen in the solution had a remarkable rise due to sludge ozonation, and 32% of released organic nitrogen was directly oxidized to NO_3^--N.

The empirical formula of activated sludge was $C_5H_7NO_2$, of which carbon and nitrogen account for about 53% and 12.4% of total dry weight respectively. Because the increase in SCOD and nitrogen was caused by the release of plasm from cell, therefore, the ratio of increased C:N should be 4.29 according to theoretical calculation. Which is to say, the ratio of increased SCOD:TN should be 11.44. Whereas, the ratio of measured increased SCOD:TN was lower than that of theoretical increased SCOD:TN at the initial stage, and this measured ratio approach zero after 2 h of ozonation. Sludge ozonation resulted in the increase in TN, whereas the increased SCOD was far lower than that of the theoretical increased SCOD (Fig. 6).

Biomass plasm flowed into solution due to cell lysis and reacted directly with ozone, part of organic carbon was oxidized to carbon dioxide. As to released organic nitrogen, which

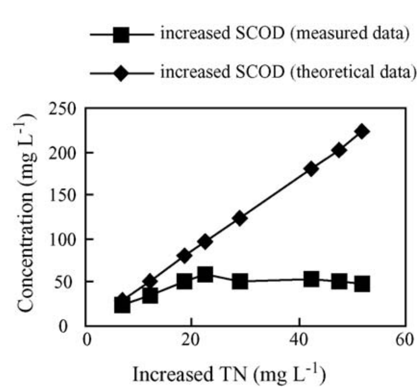

Fig. 6. Relationship between increased SCOD and increased TN during cell lysis.

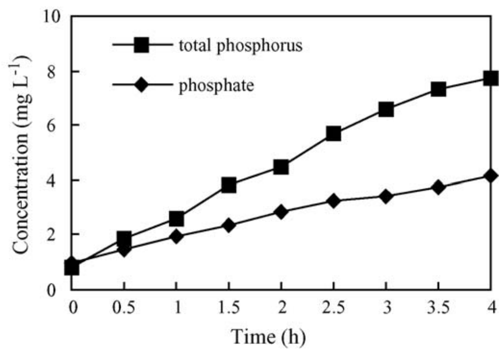

Fig. 7. Variation of PO_4^{3-}-P and TP with ozonation time.

existed in solution in a form of organic nitrogen or inorganic nitrogen and the weight was kept stable. Therefore, the ratio of increased SCOD to increased TN decreased with the extension of sludge ozonation.

3.1.4. Effect of ozonation on PO_4^{3-}-P and TP

The variation of PO_4^{3-}-P and TP in sludge mixed liquid with ozonation time is shown in Fig. 7. PO_4^{3-}-P and TP increased with the ozonation, and increased PO_4^{3-}-P accounted for 45.4% of the increased TP in 4 h of ozonation time, which indicated that a part of organic phosphorus was oxidized to phosphate. Compared with the increased TN with increased TP, it was found there was an average ratio of 6.71 in 4 h of ozonation. This ratio was slightly higher than the theoretical ratio of 5.

3.1.5. Determination of ozone dosage

Batch studies have been conducted to evaluate the effect of ozone dosage on the degree of cell lysis and hydrolysis. The aim of ozonation was to reduce excess sludge production. Therefore, ozone dosage should be determined according to the effect of ozonation on MLSS and MLVSS of the sludge. Based on the above test data depicted in Fig. 4, 2 h was considered to be an appropriate ozonation time. Ozone concentration was multiplied by ozonation time and air flow rate, then divided by SS of the sludge, and an ozone dosage of 0.16 kg O_3/kg MLSS was determined.

3.2. Continuous operation (second stage)

3.2.1. Effect of ozonated sludge flow rate on system sludge yield

Continuous operation was carried out to investigate the effect of ozonated sludge flow rate on system sludge yield. The operating conditions of above three systems were all same, and the amount of sludge to be ozonated was 0%, 2% and 4% of the reactor volume, respectively, which corresponded to 0%, 0.5% and 1% of influent flow rate Q, respectively, and these three systems were named as Nos. 1–3 systems, respectively. There was no excess sludge wastage from three systems during the experimental period.

It can be seen from Fig. 8 that MLSS in three systems kept increasing during experimental period, whereas the sludge concentration in No. 1 system increased at the highest speed, and MLSS increased from initial 2254 mg L^{-1} to 9980 mg L^{-1} in 120 days of operation. An average sludge yield of 0.130 kg MLSS/kg COD was achieved during this period. As to Nos. 2 and 3 systems, average sludge yields were 0.082 kg MLSS/kg COD and 0.039 kg MLSS/kg COD, respectively. It could be seen that the sludge yield decreased with the increase in the amount of ozonated sludge. Especially for No. 3 system, from the day 25 on, the MLSS kept nearly stable, and the average sludge yield was 0.008 kg MLSS/kg COD during days 25–120 (Fig. 9).

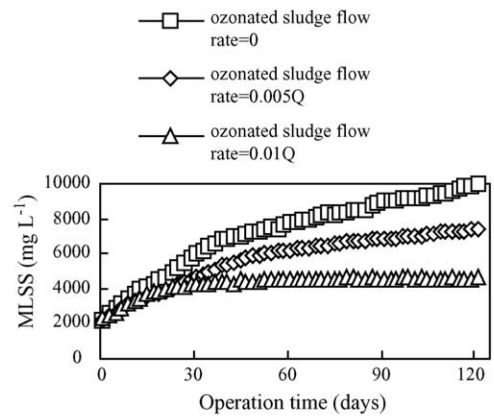

Fig. 8. Variation of MLSS in three systems.

The increase in the amount of ozonated sludge would result in a significant decrease in sludge yield, whereas the influence of ozonation on effluent quality should also be considered.

3.2.2. Effect of ozonation on effluent quality

In No. 1 system, permeate was always kept below 30 mg L^{-1} during the experimental period. With the increase of ozonated sludge flow rate, there was a rise in both permeates in Nos. 2 and 3 systems, whereas their UF membranes still kept permeate CODs less than 40 mg L^{-1}. For Nos. 1–3 systems, the average removals for COD were 91.23%, 89.86% and 88.22%, respectively. It seemed that the treatment performance was weakened due to the activated sludge ozonation, whereas considering the

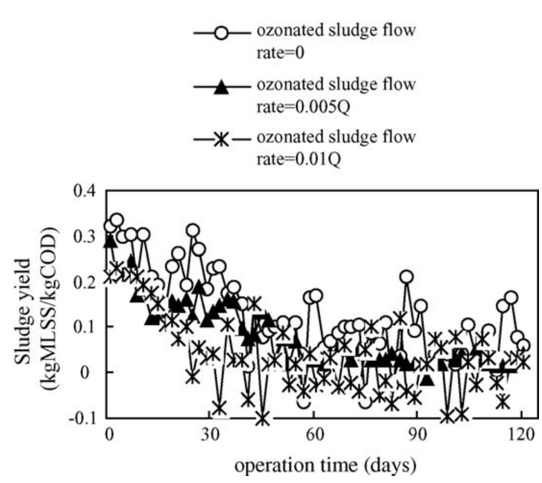

Fig. 9. Effect of the ozonated sludge flow rate on sludge yield.

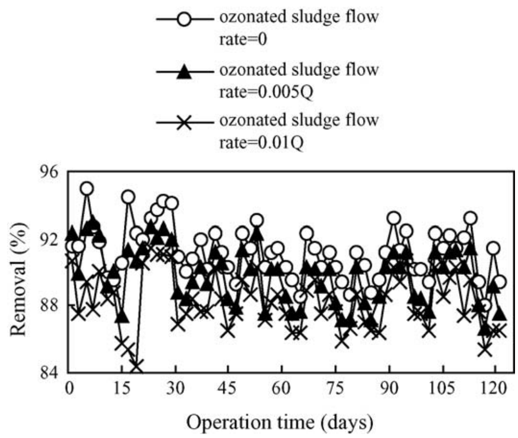

Fig. 10. Variation of COD removals in three systems.

additional organics introduced into systems by ozonation, Nos. 2 and 3 systems even removed more organics in quantity than No. 1 did. Some large molecular and refractory organics may be produced by sludge ozonation, and they could be retained by UF membrane in the reactor through size-exclusion. In addition, some easy biodegradable organics could be biologically mineralized directly. Generally, a suitable amount of activated sludge ozonation did not deteriorate the permeate COD significantly (Fig. 10).

NH_3-N concentrations in three systems were detected to investigate the influence of sludge ozonation on nitrification. The removal for NH_3-N was similar to COD removal, and the removals for NH_3-N in three systems were 94.64%, 92.94% and 91.42%, respectively. For the inflow of additional nitrogen by sludge ozonation, Nos. 2 and 3 systems have higher NH_3-N loads compared with No. 1 system. Although there were relatively higher amounts of NH_3-N in permeates in Nos. 2 and 3 systems, nitrification reactions still took place smoothly in these two systems, and NH_3-N concentrations in both permeates were less than 3 mg L^{-1} (Fig. 11).

The amounts of ozonated sludge were 2% and 4% of the reactor volume for Nos. 2 and 3 systems, respectively, which meant that these two systems have SRT of 50 days and 25 days, respectively. These two long SRTs were long enough for a complete nitrification, which was to say, small quantity of activated sludge to be ozonated and recycled into reactor would not weaken the performance of nitrification.

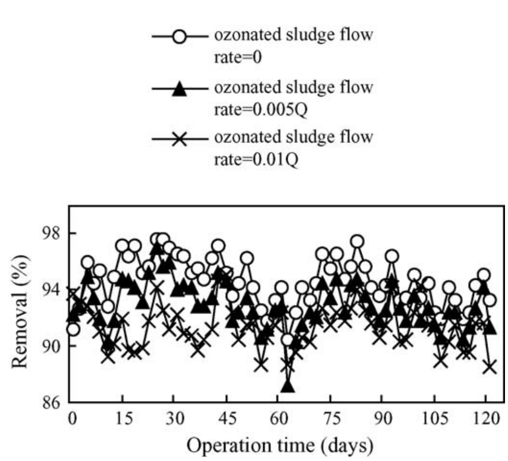

Fig. 11. Variation of NH_3-N removals in three systems.

Based on the above findings, it was concluded that the addition of sludge ozonation unit into MBR unit could reduce sludge production significantly. Meanwhile, an excellent quality of permeate could be obtained as well.

3.2.3. Economic analysis

Energy consumption cost of about 15 Yuan (RMB), equivalent to US$ 1.8, is needed to produce 1 kg of ozone gas. Based on the experimental data, the operating cost of sludge ozonation could be calculated. Taking the ozonated sludge flow rate = 0.01Q (where Q stands for influent flow rate) as an example, the MLSS in MBR was maintained at about 4000 mg L^{-1}, and ozone dosage was 0.16 kg O_3/kg MLSS. Thus, the sludge ozonation operating cost is equal to (15 Yuan/kg O_3 × 4.0 kg MLSS/m^3 × 0.16 kg O_3/kg MLSS) = 9.6 Yuan (US$ 1.15)/m^3 sludge. The flow rate of ozonated sludge was about 0.01Q; thus, the additional ozonation cost for wastewater treatment is 9.6 Yuan/m^3 × (0.01Q/Q) = 0.096 Yuan (US$ 0.0115)/m^3 wastewater, whereas in a conventional wastewater treatment plant, the handling, treatment and ultimate disposal of wasted biosolids account for from 50% to 60% of the operating costs of the plant [10], which means that sludge ozonation process could reduce the operating cost of combined wastewater and excess sludge treatment.

4. Conclusions

A series of batch studies were carried out to get an understanding of the effect of ozonation on sludge properties. It was found that the cryptic condition caused by sludge ozonation could amplify microbial cell lysis, for ozone could disrupt the cell walls and caused the release of plasm from the cells, and the amounts of soluble organics in the solution increased with ozonation time. With the rise of soluble organics, the amount of soluble organics to be mineralized increased as well, which would reduce the soluble organics content. Sludge ozonation also increased the contents of nitrogen and phosphorus in the solution, and part of organic nitrogen and phosphorus released from the cells could be oxidized to inorganic nitrogen and phosphorus. In addition, it was also found that the filamentous bacteria were squeezed and bundled after ozonation, and SVI decreased with ozonation time. On the basis of the test data, a suitable ozone dosage of 0.16 kg O_3/kg SS was determined.

Three systems were run in parallel for a period of 120 days, of which the flow rates of activated sludge to be ozonated corresponded to 0%, 0.5% and 1% of influent flow rate Q, respectively. Experimental results demonstrated that part of activated sludge ozonation could reduce sludge production significantly, and biological performance of mineralization and nitrification would not be inhibited. It was also proved that the combination of ozonation unit with MBR unit could obtain an excellent quality of permeate as well as a small sludge yield.

Economic analysis indicated that this novel process configuration could treat both the wastewater and activated sludge effectively and economically. On the basis of obtaining high quality of effluent, an additional ozonation operating cost for treatment of both the wastewater and excess sludge was only 0.096 Yuan (US$ 0.0115)/m^3 wastewater.

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