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Performance of membrane bioreactor (MBR) system with sludge Fenton oxidation process for minimization of excess sludge production

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ABSTRACT

The study reports the minimization of excess sludge produced in the membrane bioreactor (MBR) coupled with a sludge Fenton oxidation (oxidation using H_2O_2 with an iron catalyst) process. Total experimental period was divided into two stages. At the first stage, a series of batch studies were carried out to elucidate the parameters governing the activated sludge disintegration. It was found that Fenton oxidation can disrupt the cell walls and cause the release of plasm from the cells, thus increasing the content of soluble organics and soluble nitrogen in the solution. At the following stage, two MBRs with and without the Fenton process were operated to evaluate the influence of sludge Fenton oxidation on the sludge yield and water quality. It was demonstrated that the incorporation of Fenton process can significantly reduce sludge production, as evidenced from the decrease in the value of the average sludge yield from 0.15 to 0.006 g MLSS/g COD. The water quality of effluent in both systems was maintained at a satisfactory level. Furthermore, it was revealed that the MBR system with the sludge Fenton oxidation process showed relatively better performance for TN removal than that without it.

1. Introduction

Activated sludge has been widely applied to treat wastewater due to its advantages including low running cost and high degradation efficiency. The disposal of the excess biomass produced during the biological treatment of wastewater mainly contribute to its total operation costs reaching as high as 50–60% [1]. Hence, there is considerable research on the techniques of excess sludge treatment, many sludge reduction techniques have been previously proposed [2–8]. Among them, one promising concept is to achieve zero discharge of excess sludge by coupling with disintegration in biomass recycle system. With respect to the various techniques developed for wastewater sludge disintegration [8,9], chemical-enhanced processes such as, ozonation, alkaline addition and chlorination shows the potential of industrial application [10].

Recently, special attention has been devoted to the indirect oxidation process called Fenton due to its outstanding performance in the destruction of organic pollutant contained in wastewaters, sludge, and contaminated soils [11]. In this process, reactions between the Fenton's reagent such as H_2O_2 and Fe^{2+} produce the hydroxyl radicals which are able to oxidize the organic pollutants [12,13]. For example, Lu et al. [14] reported that the Fenton technology can be used to improve the dewatering of activated sludge. Tokumura et al. [15] found that the photo-Fenton process is one of the feasible processes for disintegration of excess activated sludge.

The membrane bioreactor (MBR) process has recently been developed to wastewater treatment due to its unique advantages including improved effluent quality, high mixed liquor suspended solids (MLSS), low system volume and long sludge retention time (SRT) [16,17]. Material balance on chemical oxygen demand (COD) in the 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 [18].

In the present study, we examined the minimization of excess sludge produced in the MBR with the help of the sludge Fenton oxidation. The mechanism of such a process involves (i) the drainage of the excess sludge into a Fenton reactor in which the death and lysis of biomass was degraded by hydroxyl radicals produced from the Fenton reactions; (ii) the recycling of the treated sludge to the MBR as substrates for further metabolism. The aim of the work is to reduce the production of sludge by incorporating the sludge Fenton oxidation into MBR.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up consisted of a membrane bioreactor (MBR) system and a batch Fenton oxidation system, as shown in Fig. 1. For comparison, a control set-up which contains only the

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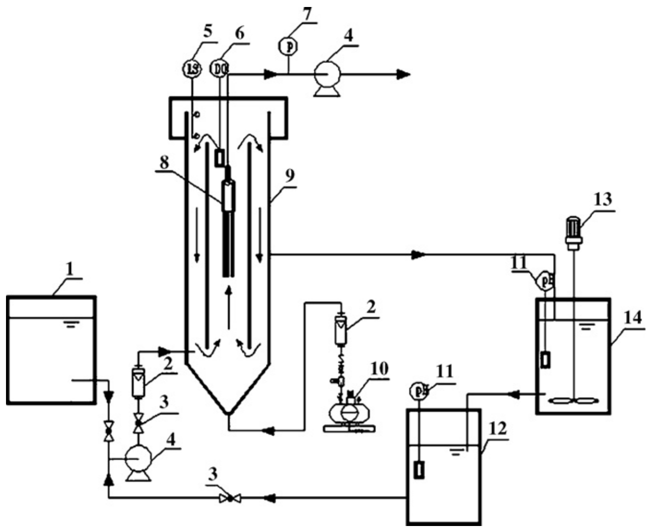

Fig. 1. Schematics of the MBR system coupled with sludge Fenton oxidation process: (1) feed tank; (2) flowmeter; (3) valve; (4) pump; (5) liquid level controller; (6) dissolved oxygen meter; (7) pressure gauge; (8) membrane module; (9) bioreactor; (10) air compressor; (11) pH meter; (12) sludge storage tank; (13) machine mixer; (14) Fenton oxidation reactor.

MBR system (without the Fenton oxidation process) was also operated. During the Fenton oxidation run, the sludge was drawn from the MBR and recirculated into the MBR through a pump after the Fenton oxidation process. Before it was recirculated into the MBR, the solution of the sludge Fenton oxidation was adjusted to pH 7.0 with sodium hydroxide. The operational conditions are listed in Table 1. The MBR system was operated with a flow rate of 20 L day^{-1}. The hydraulic retention time (HRT) of MBR was 8 h. A hollow fiber polyethylene membrane with 0.1 μm of pore size was used. The surface area of the membrane module was 0.5 m^2. A synthetic wastewater, which was prepared by mixing tap water with certain quantities of starch, glucose, NH_4Cl, Na_2HPO_4, NaH_2PO_4, $NaHCO_3$ and Na_2CO_3, was used in this study; Table 2 summarized its characteristics.

The total experimental period was divided into two stages. At the first stage, a series of batch studies were carried out to elucidate the parameters governing the activated sludge disintegration by the Fenton oxidation process. At the following stage, two membrane bioreactors (MBRs), one with a batch sludge Fenton oxidation and the other without it, were operated in parallel for a long period to evaluate the influence of sludge Fenton oxidation on the sludge yield and water quality.

Table 1
Operating parameters of the MBRs.

Items	Fenton's oxidation run	Control run
Working volume (L)	6.7	6.7
Influent flow (L day^{-1})	20	20
DO (mg L^{-1})	1.5±0.2	1.5±0.2
HRT (h)	8	8
SRT (day)	No wasting	No wasting
Sludge Fenton's oxidation (L day^{-1})	0.13	0
Pore size of membrane (μm)	0.1	0.1
Surface area of module (m^2)	0.5	0.5
Flux (L m^{-2} h^{-1})	20	20

Table 2
The characteristics of the synthetic wastewater.

Parameter	Range	Mean
pH	6.8–7.5	7.1
SS (mg L^{-1})	82–113	98
COD (mg L^{-1})	830–880	855
NH_3-N (mg L^{-1})	42–54	48
TN (mg L^{-1})	54–73	64
TP (mg L^{-1})	3.4–5.1	4.3

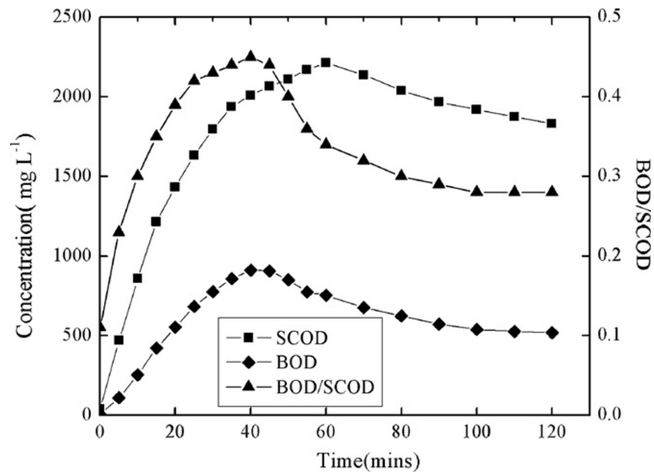

Fig. 2. The variation of SCOD, BOD and BOD/SCOD with Fenton oxidation time.

2.2. Fenton oxidation process

Samples of excess sludge (200 mL) were batch-treated in a beaker of 500 mL at fixed operating conditions. The treatment was performed by firstly adding H_2SO_4 (98%) to adjust the pH to 3, then adding $FeSO_4$ (10%) and H_2O_2 (30%). The oxidation reaction takes place at the ambient temperature and pressure. The mixture was stirred at 100 rpm. The reaction was stopped when the change of mixed liquor suspended solids (MLSS) is insignificant. Samples (l mL) from the liquid phase were taken at predetermined time intervals using a syringe. In order to remove fine solids, samples were filtered through 0.45 μm millipore filter for subsequent analysis.

2.3. Analysis methods

COD, BOD, TP, NH_3-H, NO_3^--N, TN, MLSS and mixed liquor volatile suspended solids (MLVSS) were analyzed using standard methods [19]. Soluble COD (SCOD) samples were obtained by filtrating the mixed liquor through a 0.45 μm millipore filter. The pH was measured with a pH meter (pHS-3C, China). Dissolved oxygen (DO) and temperature were determined by a portable DO meter combined with a temperature probe (JBP-607 DO, China).

All the tests were repeated three times under the identical conditions. The reported data in this study were the means of the triplicate measurements. Standard deviations were calculated from three independent measurements and found to be less than 5%.

3. Results and discussion

3.1. Fenton oxidation process (first stage)

3.1.1. Sludge disintegration

Fig. 2 shows the typical data for reducing activated sludge by the Fenton oxidation process. The initial concentrations of sludge, Fe^{2+} and H_2O_2 were 8600, 200 and 8000 mg L^{-1}, respectively, and the initial solution pH was 3. It was observed that the treatment resulted in the color change from the dark brown color (the activated sludge slurry before disintegration) to pale gray (the degraded samples). The microscope observation indicated that the number and size of activated sludge flocs were

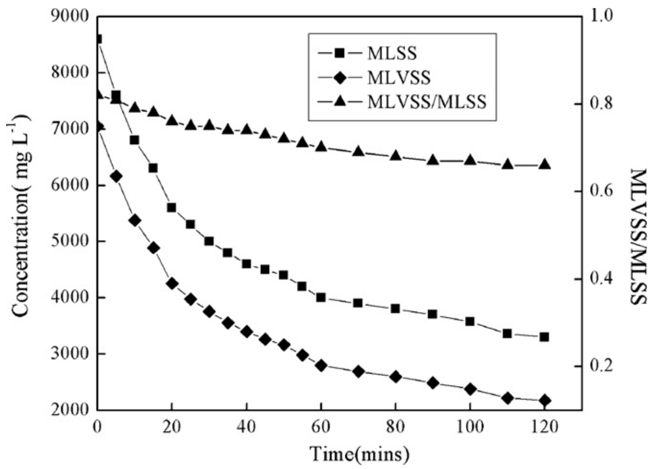

Fig. 3. The variation of MLSS, MLVSS and MLVSS/MLSS with Fenton oxidation time.

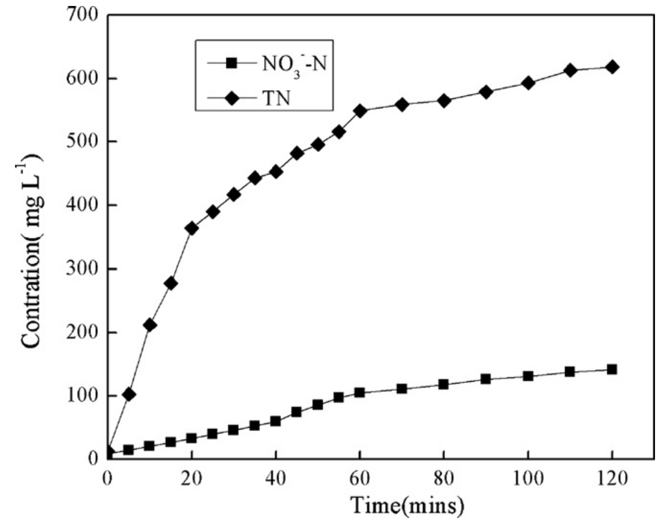

Fig. 4. The variation of NO_3^--N and TN with Fenton oxidation time.

decreased by the Fenton oxidation process, in accordance with the observations for the sludge minimization by ozonation [20], mechanical disruption [21], UV light photo-Fenton reaction [15] and the solar photo-Fenton reaction [22]. It can be seen from Fig. 2 that SCOD increased from 38 to 2213 mg L^{-1} during the initial 60 min of the Fenton oxidation process, and decreased at a slow rate to 1832 mg L^{-1} during the following time. BOD reached its maximum value of 607 mg L^{-1} from initial 4.2 mg L^{-1} during the initial 40 min. BOD/SCOD increased from 0.11 to 0.45 after 40 min of the Fenton oxidation process and thereafter decreased to around 0.31. As described above, the solubilization of excess sludge was carried out in two steps. In the first step, some activated sludge microorganisms were mainly killed and oxidized to dissolved organic substances by the Fenton oxidation process. As a result of the oxidation, organic substances were leached into the supernatant, and the SCOD increased. With the increase of soluble organics, the amount of soluble organics to be oxidized increased as well. This would reduce the soluble organics content. In the second step, the oxidation of dissolved organic substances by the Fenton oxidation process might be dominant. On one hand, sludge Fenton oxidation increased the amount of soluble organics; on the other hand, the increase of SCOD supplied more chances for the reaction between Fenton's reagent 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 [23]. After 90 min, they might be comparable to each other and the change in SCOD was insignificant. The variation of BOD can be explained by the fact that a part of organics released from cell walls was biodegradable, which resulted in the increase of BOD as well as BOD/SCOD during the initial 40 min. It appears that the Fenton oxidation converted the sludge into various forms of easily biodegradable organic matter, such as volatile fatty acids and low molecular weight compounds [24]. At the following 20 min of the Fenton oxidation process, a part of BOD was oxidized, whereas SCOD increased in this period. Therefore, BOD/SCOD decreased from 0.45 to 0.31. During the reaction period from 90 to 120 min, the amount of BOD newly released from the cells was approximately equal to that of being oxidized, leading to a relative stable BOD determined.

3.1.2. *Effect of the Fenton oxidation process on MLSS and MLVSS*

Fig. 3 shows the decrease of MLSS and MLVSS with the increase of reaction time during the 120 min of the Fenton oxidation process. It was noted that the MLSS decreased from 8600 to 3300 mg L^{-1}, and MLVSS/MLSS decreased from 0.85 to 0.66. Based on these data, it can be deduced that the decrease in MLSS was mainly due to the decrease in MLVSS. The aim of the Fenton oxidation process was to reduce excess sludge production; therefore, the reaction time should be determined according to the effect of the Fenton oxidation process on MLSS and MLVSS of the sludge. It can be seen from Fig. 3 that the optimum time required was 90 min.

3.1.3. *Effect of the Fenton oxidation process on nitrogen*

During the sludge disintegration by the Fenton oxidation process, the variations of NH_3-N and NO_2^--N were insignificant (data not shown), but a significant rise in concentrations of NO_3^--N and TN were clearly visible (in Fig. 4). During the 120 min of the Fenton oxidation process, NO_3^--N increased from 9.6 to 142 mg L^{-1}, and TN increased from 13 to 618 mg L^{-1}. Therefore, the organic nitrogen in the solution had a remarkable rise due to sludge Fenton oxidation process, and 23% of the 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. Cell lysis released cell contents into the sludge slurry and contributed to the organic loading. In other words, because the increase in SCOD and TN was caused by the release of plasm from cell, the ratio of increased SCOD/TN should be 11.44. However, it can be seen from Fig. 5 that the mea-

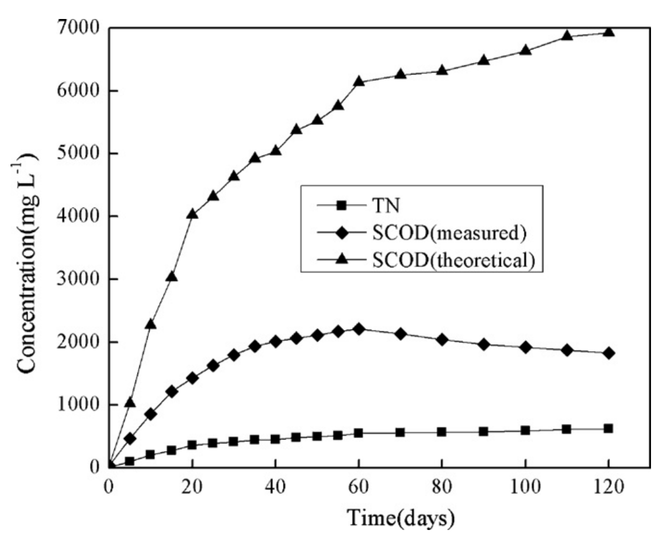

Fig. 5. The variation of SCOD and TN with Fenton oxidation time.

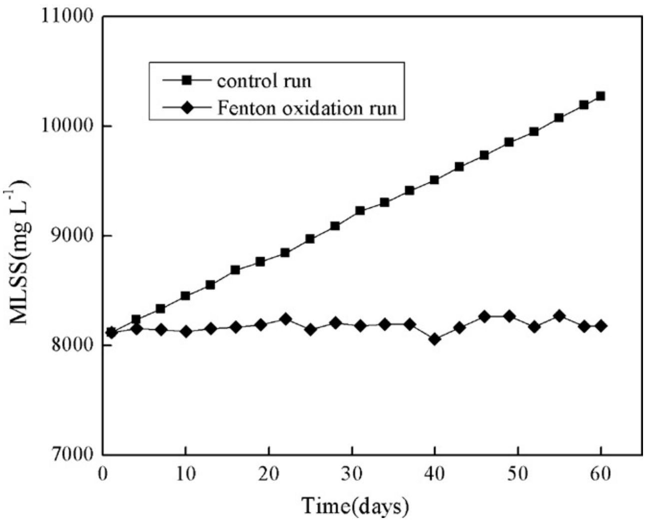

Fig. 6. The variation of MLSS in the MBRs.

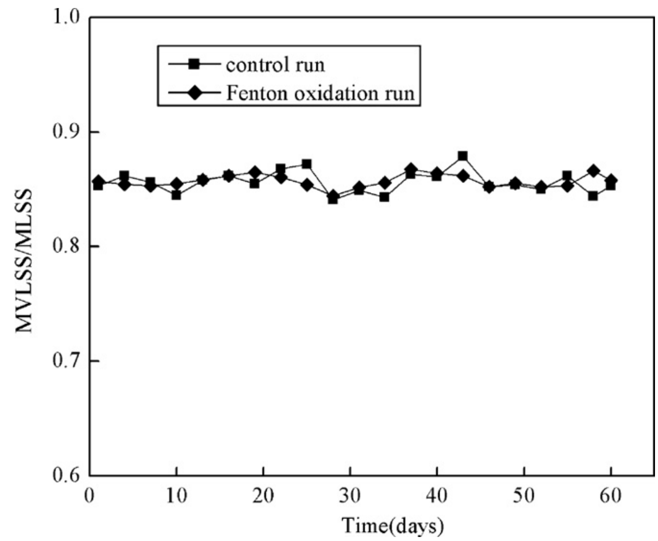

Fig. 7. The variation of MLVSS/MLSS in the MBRs.

sured SCOD was lower than the theoretical SCOD, and the increase of the measured SCOD approach zero after 60 min of the Fenton oxidation process. Therefore, measured ratio of increased SCOD/TN was lower than that of the theoretical value. Fenton oxidation converted the sludge into various forms of easily biodegradable organic matter, such as volatile fatty acids and low molecular weight compounds, and part of organic carbon was oxidized to carbon dioxide. As to released organic nitrogen, which existed in solution in a form of organic nitrogen or inorganic nitrogen, its weight was kept stable. Therefore, the value of SCOD/TN decreased with the extension of sludge Fenton oxidation.

3.2. Continuous MBR operation (second stage)

3.2.1. Reduction of excess sludge production

In order to investigate effects of sludge Fenton oxidation on system sludge yield and reduction of excess sludge production, the amount of MLSS in the reactor was measured. There was no excess sludge wastage from two systems during the experimental period.

It can be seen from Fig. 6 that the MLSS of the control experiment (without sludge Fenton's oxidation) continuously increased because of the accumulation of excess sludge, and MLSS increased from 8120 to 10270 mg L^{-1} during 60 days of operation. An average sludge yield of 0.15 g MLSS/g COD was achieved during this period. The value of sludge yield was relatively low compared to 0.40 g MLSS/g COD in the previous study [25]. The MBR system with the very long SRT was relatively effective on the reduction of sludge production. However, in the Fenton oxidation run, the MLSS was nearly stable and the average sludge yield was 0.006 g MLSS/g COD in 60 days of operation. It thus can be concluded that the application of the sludge Fenton oxidation to the MBR was significantly effective for the minimization of excess sludge production. The variations of MLVSS/MLSS in the MBR are shown in Fig. 7. The MLVSS/MLSS in the control and the Fenton oxidation runs maintained at 0.85 constantly for the experiment periods. It was observed that the accumulation of inorganic from the sludge Fenton oxidation in the reactor was insignificant and the organic matter from the sludge Fenton oxidation was easily degraded in the MBR [24].

3.2.2. Effect of Fenton oxidation on effluent quality

The effluent CODs of two experiments were recorded (Fig. 8). They were maintained at a satisfactory level in both runs (less than 50 mg L^{-1}). The average ratio of COD removal corresponding to system with and without the Fenton process was calculated to be 94.9% and 96.2%, respectively. Considering the additional organics introduced into systems by the Fenton oxidation process, the system with the sludge Fenton oxidation had higher organic loads. It showed that the system with the sludge Fenton oxidation operated successfully without sludge wasting and further accumulation of non-biodegradable compounds in the reactor.

To investigate the influence of sludge Fenton oxidation on nitrification, the NH_3-N and TN concentrations in two systems were detected. It can be seen from Fig. 9 that NH_3-N concentrations of the effluent in two systems were less than 3 mg L^{-1}, and TN concentrations of the effluent in two systems were less than 14 mg L^{-1}. The average ratio of NH_3-N removal in systems with and without Fenton reactions was 94.3% and 96.1%, respectively. For the additional nitrogen from the sludge Fenton oxidation, the system with the sludge Fenton oxidation had higher NH_3-N loads. The average TN removal efficiencies for the control and the Fenton oxidation run were 79.7% and 82.8%, respectively. Such differences in the TN removal might be due to the addition of soluble organic matter in the Fenton reaction run as a carbon source for the TN removal.

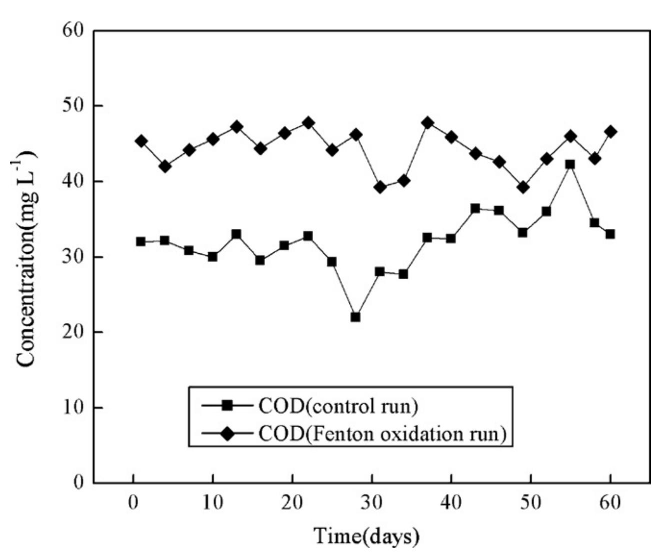

Fig. 8. The variation of effluent COD in the MBRs.

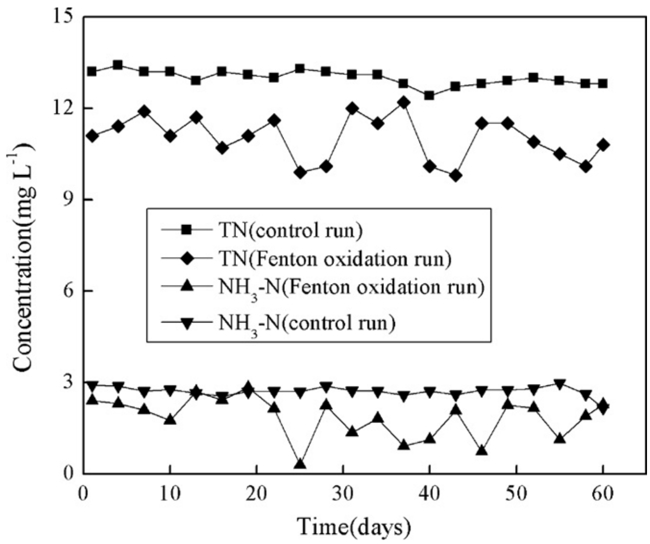

Fig. 9. The variation of effluent NH_3-N and TN in the MBRs.

4. Conclusions

A series of batch studies were carried out to understand performances of the sludge Fenton oxidation process. It was found that the solubilization of excess sludge by the Fenton oxidation process could be divided into two phases. At the beginning of the Fenton oxidation process, cell lysis released cell contents into the sludge slurry, as a result, the MLSS decreased from 8600 to 3300 mg L^{-1} and the SCOD concentration in the solution increased. The SCOD reached the maximum and then decreased, in accordance with the phenomenon for the sludge disintegration by UV light photo-Fenton reaction [15]. In this period, the oxidation of soluble organic substances by Fenton reaction might be dominant. Sludge Fenton oxidation also increased the contents of nitrogen in the solution and about 23% of the released organic nitrogen was directly oxidized to NO_3^--N. The measured ratio of increased SCOD/TN was lower than the theoretical value.

Effects of the sludge Fenton oxidation on the reduction of excess sludge production and the enhancement of pollutant removal in MBR were evaluated. In the control run (without sludge Fenton oxidation), the average sludge yield was 0.15 g MLSS/g COD during 60 days of operation. However, in the Fenton oxidation run, the MLSS kept nearly stable, and the average sludge yield was 0.006 g MLSS/g COD during 60 days of operation. In addition, the value of MLVSS/MLSS in both systems maintained at 0.85 constantly for the experiment periods. The water quality of the effluent achieved a satisfactory level in both systems. Furthermore, the performance of TN removal with the sludge Fenton oxidation was relatively better than that without it. It was revealed that the sludge was degraded in the Fenton reactor and successfully used as a carbon source. Application of this sludge Fenton oxidation to the MBR system was significantly effective for the minimization of excess sludge production as well as for the enhancement of TN removal.

Acknowledgments

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