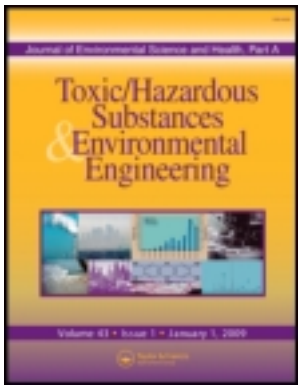

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BIOLOGICAL NUTRIENT REMOVAL

Nitrification–Denitrification of Opto-electronic Industrial Wastewater by Anoxic/Aerobic Process

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ABSTRACT

This research focused on the biological treatment of high-strength organic nitrogen wastewater, and presented the results from the nitrification and denitrification of an actual industrial wastewater using anoxic/aerobic process. The opto-electronic industrial wastewater often contains a significant quantity of organic nitrogen compounds and has a ratio over 95% in organic nitrogen (Org-N) to total nitrogen (T-N). In this study, a 2-stage anoxic/aerobic process was established and evaluated the efficiency of wastewater treatment. Raw wastewater from an actual TFT-LCD manufacturing plant was obtained as the sample for looking into the feasibility of opto-electronic industrial wastewater treatment. After toxicity identification evaluation (TIE) test of raw wastewater, the inhibition was related to organic nitrogen (TMAH, MEA) and unionized ammonia (free ammonia, NH_3) with high pH. Therefore, pH control is important for biological treatment of high-strength organic nitrogen industrial wastewater. Besides, hydraulic retention time (HRT) and mixed liquor recycled rate (MLR) were controlled independently to distinguish between the effects of these two factors. Under suitable HRT (>1.7 d) and mixed liquor recycled rate ($<4Q$), effluent of NH_4-N, NO_3-N + NO_2-N, and COD can fall below 20 mg/L, 30 mg/L, and

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80 mg/L. The anoxic/aerobic process removed 92–98% of the carbon source, and approximately 80% of TKN, 70% of T-N.

Key Words: Biological treatment; Denitrification; Industrial wastewater; Nitrification.

INTRODUCTION

The opto-electronic industry, developed very fast over the past decade in the world, is a high technological manufacturing. Many countries concentrate on its development because of the demand for these products increase quickly. A number of opto-electronic industries, such as TFT-LCD (Thin Film Transistor Liquid Crystal Display) manufacturing plants, consist of the following manufacturing processes: (1) array, (2) color filter, and (3) liquid crystal. All of these steps need large quantities of organic solvent as developers, strippers and rinses, result in the discharge of large amounts of wastewater. In addition to organic carbon, the wastewater often contains a significant quantity of organic nitrogen, such as ethanolamine, (MEA, $C_2H_5ONH_2$) and tetra-methyl ammonium hydroxide (TMAH, $(CH_3)_4NOH$). In according to meet stringent discharge standards, biological nitrogen removal process, consisting of nitrification and denitrification, is one of the most promising methods to remove nitrogen from wastewater. Biological nutrient removal processes accelerated significantly over the past decade due to more stringent nutrients (nitrogen and phosphorus) discharge limits being imposed on wastewater treatment plants. Moreover, biological treatment is relatively cheap and produces no unwanted side-products.

Nitrification is a two-step, aerobic and autotrophic process used for conversion of ammonium to nitrate (NO_3-N). Ammonium is converted to nitrite (NO_2-N) by *Nitrosomonas* species in the first step, and nitrite is converted to nitrate by *Nitrobacter* species in the second. The nitrification of the biological nitrogen removal process is generally recognized as the most vulnerable activated sludge process, both nitrifying species in this commensalystic system are very sensitive to operation conditions (such as pH, temperature, dissolved oxygen (DO), substrate, and also chemical oxygen demand (COD)).[1] In order to reach the maximum nitrification rate, each of those parameters has to lie within a specific interval. For example, the temperature, which mostly could not be influenced, should be between 28 and 33°C. With regard to pH and oxygen it is well known that the nitrification has an optimum in the 7–8 pH range and the nitrifying organisms are sensitive to low oxygen concentration below 1 mg L^{-1}.[2] Denitrification is an anoxic, heterotrophic process used for conversion of nitrate to nitrogen gas by denitrifying organisms. Denitrifying organisms require external carbon source for biosynthesis and energy generation.

Thus, the effectiveness of biological nitrogen removal processes depends on the ability of nitrifying and denitrifying organisms. Numerous studies investigate the interactive factors that affect nitrification and denitrification in municipal wastewater.[3–7] However, industrial wastewater usually contains high-strength nitrogen and specific organic compounds that might inhibit the activity of the organisms.[8] The opto-electronic industrial wastewater, differs from the animal

production plants and municipal wastewater, has a ratio over 95% in organic nitrogen (Org-N) to total nitrogen (T-N), in particular. Therefore, biological nitrogen removal efficiency may have a significant effect resulting from opto-electronic industrial wastewater. The application of biological nitrogen removal process in treatment of opto-electronic industrial wastewater is still in its infancy.

The purpose of this study is to investigate the biological treatment of high-strength organic nitrogen opto-electronic industrial wastewater without dilution, and to explore the nitrogen removal capabilities of anoxic/aerobic process. Hydraulic retention time (HRT) and mixed liquor recycle rate (MLR) were controlled independently to distinguish between the effects of these two factors.

METHODS

Characterization of Wastewater

Raw wastewater was collected from an actual TFT-LCD plant and stored at 4°C in refrigerator until used in experiments. The wastewater chemical oxygen demand (COD) concentration varied from 500 to 2500 mg/L, total nitrogen (T-N) concentration varied from 100 to 300 mg/L, organic nitrogen (Org-N) concentration varied from 95 to 295 mg/L, and pH value is about 10–11 (see Table 1).

In order to prevent inhibition of nitrification and denitrification, the pH was automatically controlled between 7 and 8 in each tank, and the temperature was maintained thermostatically at 30°C using a water bath. Raw wastewater was fed into the pH adjustment tank by variable speed peristaltic pump and mixed with circulated liquid before fed into anoxic tank. A stirrer mechanically mixed the anoxic tank with a rotation speed of 100 rpm. Aeration at the bottom of aerobic tank kept the contents well-mixed and aerated (DO > 2.0 mg/L) through porous diffuser stones. Mixed liquor was recycled from aerobic tank to anoxic tank through a peristaltic pump (Fig. 1).

Table 1. Main components and quality of raw wastewater used in this study.

Items	Stripper	Developer	Rinse	Average
Main components	$(CH_3)_2SO$ (DMSO) $C_2H_5ONH_2$ (MEA)	$(CH_3)_4NOH$ (TMAH)	$CH_3CHOOHCH_3$ (IPA)	—
pH	9–11	10–13	4–10	10–11
SS(mg/L)	< 10	< 10	< 10	< 10
COD(mg/L)	800–1500	100–600	500–3700	1000–1300
TKN(mg/L)	70–300	90–150	90–240	140–160
NH_4-N(mg/L)	0–15	2–15	0.1–10	2
NO_3-N*(mg/L)	0.1–0.4	0.0–0.3	0.1–1.3	0.2

*NO_3-N = NO_3-N + NO_2-N.

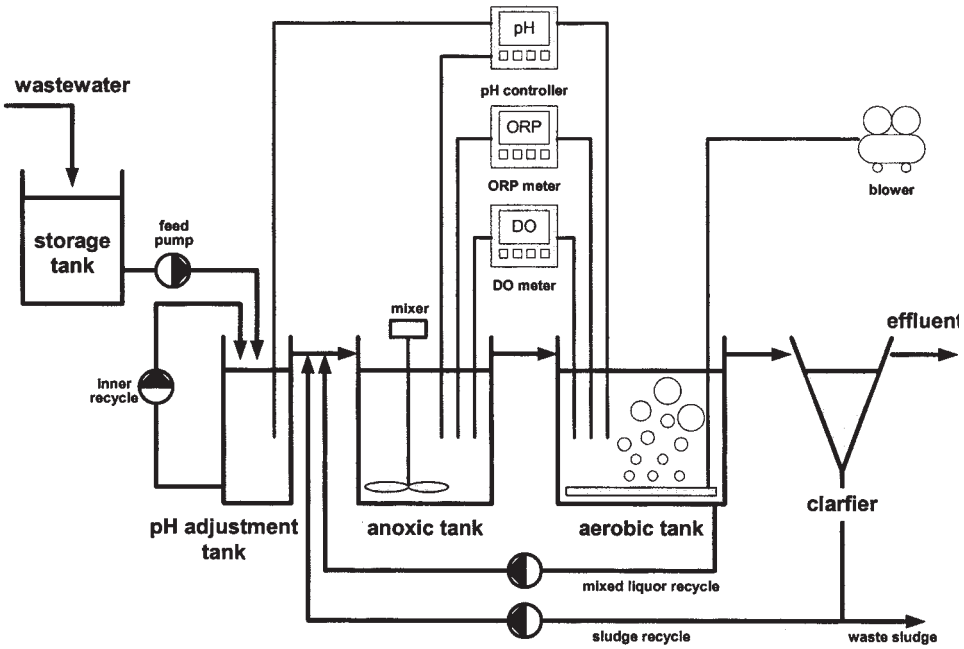

Figure 1. Schematic diagram of the anoxic/aerobic process.

Operation Condition

This study was conducted for more than 300 days, and the operating conditions of each run are summarized in Table 2. The theoretical HRT in anoxic and aerobic tanks was determined based on the influent flow rate of the system. The feeding rate was increased step-wise and the effect of HRT on performance was investigated. The effect of HRT was examined as runs 1, 2, 3, 4, 5, 6, 7, and 8. The effect of mixed liquor recycle rate was examined as runs A, B, C, D, and E. Before determining treatment efficiency, each run was maintained for a period equal to at least three times the solids retention time (SRT) (>75 days).

Monitoring and Analysis

The pH, DO, ORP, temperature, and flow rate of reactor were monitored daily. Dissolved oxygen (DO) was manually monitored with a DO analyzer (Oriental electric Co., Japan), and was maintained at higher than 2.0 mg/L in aerobic tank. Submerged oxidation–reduction potential (ORP) electrodes (Mettler Toledo Co.) monitored the oxidation–reduction potential (-1999 to $+1999$ mV) in each tank. The toxicity of wastewater was determined by the method of toxicity identification evaluation (TIE)[9] using a Microtox (Microtox Model 500, Microbics Co.). The influent, effluent, and supernatants of each tank were sampled two to three times per week. The supernatant samples were filtrated through a membrane of

Table 2. Operational conditions of experimental runs.

Run	Flow rate (L d^{-1})	Mixed liquor recycled rate	COD loading* (g L^{-1} d^{-1})	TKN loading† (g L^{-1} d^{-1})	COD/TKN ratio	HRT (days)	Actual anoxic tank HRT (h)	Average SRT (days)
1	5.76	3	0.22 (976.0)	0.026 (114.0)	8.46	4.25	—	25
2	8.64	3	0.37 (1058.8)	0.051 (147.3)	7.25	2.83	—	25
3	11.52	3	0.41 (878.8)	0.064 (136.9)	6.40	2.12	—	25
4	14.40	3	0.98 (1680.0)	0.097 (166.5)	10.09	1.70	—	25
5	21.60	3	2.06 (2345.0)	0.097 (110.1)	21.29	1.13	—	25
6	36.00	3	1.94 (1325.3)	0.170 (115.9)	11.43	0.68	—	25
7	46.08	3	1.91 (1012.3)	0.242 (128.9)	7.85	0.53	—	25
8	86.40	3	4.37 (1242.0)	0.370 (105.2)	11.81	0.28	—	25
A	11.52	2	0.29 (617.5)	0.114 (243.8)	2.53	2.12	4.02	25
B	11.52	3	0.41 (878.8)	0.064 (136.9)	6.41	2.12	3.02	25
C	11.52	4	0.46 (982.3)	0.063 (134.7)	7.29	2.12	2.42	25
D	11.52	5	0.58 (1254.2)	0.129 (275.0)	4.56	2.12	2.01	25
E	11.52	6	0.48 (1024.6)	0.059 (125.0)	8.19	2.12	1.72	25

*The COD concentration in the influent is shown in parentheses.
†The TKN concentration in the influent is shown in parentheses.

0.45 μm. The analysis of various constitutes and the measurements of parameters of interest were performed in accordance with the standard methods[10] and the corresponding instrument instruction manuals. The constituents of most interest were total nitrogen (T-N), total kjeldahl nitrogen (TKN), nitrate (NO_3-N), nitrite (NO_2-N), chemical oxygen demand (COD), total organic carbon (TOC), biochemical oxygen demand (BOD_5), and total and volatile suspended solids (TSS and VSS).

RESULT AND DISCUSSION

Wastewater Assay

The nitrification process is susceptible to inhibition caused by toxic compounds in the influent. Toxic loads in the influent can result in reduced nitrogen removal in the plant. For this reason, before designing a biological treatment system in industrial wastewater, it is important to identify what organic compounds that might inhibit the ability of nitrifying and denitrifying organisms. The toxicity identification evaluation (TIE) was used to investigate to what extent substances were able to inhibit nitrification. The results of TIE are summarized in Table 3.

Table 3 shows that developer, which had a toxicity unit (T.U) value of 68.7, was the most potent inhibitor. After aeration, filtration, adding EDTA, and adding $Na_2S_2O_4$, the T.U. values were 16.88, 16.86, 16.19, and 16.17 respectively. The results suggest that the wastewater did not contain volatile compounds, solids, heavy metals, and oxidants that might cause inhibition. Furthermore, the toxicity

Table 3. Toxicity identification evaluation of the wastewater.

	Wastewater	
Item	EC50 (%)	T.U.
Baseline	5.336	18.74
Stripper	4.154	24.07
Developer	1.456	68.70
Rinse	> 100 (0.219)*	—
Raw wastewater	5.942	16.89
After aeration	5.924	16.88
After filtration	5.931	16.86
Add EDTA	5.497	16.19
Add $Na_2S_2O_4$	5.503	16.17
Adjust pH = 7	> 100 (0.104)	—
Adjust pH = 3	> 100 (0.150)	—
SPE1 filtration**	5.446	16.36
SPE2 filtration	7.118	14.05
SPE3 filtration	> 100 (0.195)	—
SPE4 filtration	> 100 (0.003)	—
Effluent	> 100 (0.305)	—

*The inhibition rate of *Photobacterium phosphoreum* is shown in parentheses, if EC50 (%) > 100.
**After filtrated by solid phase extraction (SPE) tube 1, the filtrate was adsorbed by SPE2, SPE3, and SPE4.

disappeared after the wastewater were adjusted pH to 7 and filtrated through SPE 2. This suggests that the inhibition was related to organic nitrogen (TMAH, MEA) and unionized ammonia (free ammonia, NH_3). It can be seen from the components of wastewater (Table 1). The pH (10–11) of the wastewater also was related to a greater percentage of the ammonia being present in the inhibitory unionized form. Thus, it is evident that pH control is vital for nitrification and denitrification of high-strength industrial wastewater. Controlling the pH between 7 and 8 in pH adjustment tank can minimize inhibition of nitrifiers by unionized ammonia or unionized nitrous acid.

Effect of HRT

The operational performance of each run is summarized in Table 4. In runs 1, 2, 3, 4, 5, 6, 7, and 8, over 90% of the COD was removed, but effluent TKN increased with decreasing HRT (Fig. 2 and Fig. 3). This tendency is reasonable and is predicted by the kinetic theory. As shown in Fig. 2, it indicated that the COD removal percentage increased in anoxic tank and decreased in aerobic tank with decreasing HRT. When the HRT was further decreased to 1.7 d, the COD removal percentage remained unchanged at about 65–68% in anoxic tank and 20–25% in aerobic tank. In runs 1, 2, and 3, a lack of sufficient nitrate and nitrite to denitrify (Fig. 4), the COD removal percentage in anoxic tank was under 50%. Nevertheless,

Table 4. Operational performance of experimental runs.

Run	HRT (Days)	COD			TKN			NO_3-N	NH_4-N	T-N		
		Influent (mg/L)	Effluent (mg/L)	Removal (%)	Influent (mg/L)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Removal (%)
1	4.25	976.0	52.7	95.5	114.0	10.7	90.6	10.7	5.2	114.5	21.4	81.3
2	2.83	1058.8	34.8	96.7	147.3	14.8	91.3	29.3	7.6	147.7	44.1	70.2
3	2.12	878.7	53.4	93.9	136.9	27.0	77.4	26.7	6.6	137.4	53.8	60.9
4	1.70	1680.0	44.0	97.4	166.5	24.2	80.6	19.6	12.4	166.6	43.7	73.8
5	1.13	2345.0	82.0	96.5	110.0	31.0	71.8	25.3	12.9	110.0	56.3	48.9
6	0.68	1325.3	40.3	97.0	115.9	52.2	54.9	18.8	42.6	116.2	72.7	37.4
7	0.53	1012.3	50.0	95.1	128.9	75.2	41.6	8.8	56.6	130.3	84.0	35.5
8	0.28	1242.0	111.8	91.0	105.2	74.2	29.4	3.8	50.6	107.0	78.0	27.1
A	2.12	617.5	35.0	94.3	243.8	78.9	67.6	32.8	5.6	245.3	110.9	54.7
B	2.12	878.7	53.4	93.9	136.9	27.0	77.4	26.7	6.6	137.4	53.8	60.9
C	2.12	982.3	74.0	92.5	134.7	30.9	77.1	3.6	4.4	134.9	33.7	75.0
D	2.12	1254.2	102.5	91.8	275.0	147.7	46.2	2.2	127.3	275.4	150.3	45.6
E	2.12	1024.6	122.0	88.1	275.0	192.8	29.8	1.2	190.3	275.4	196.0	28.8

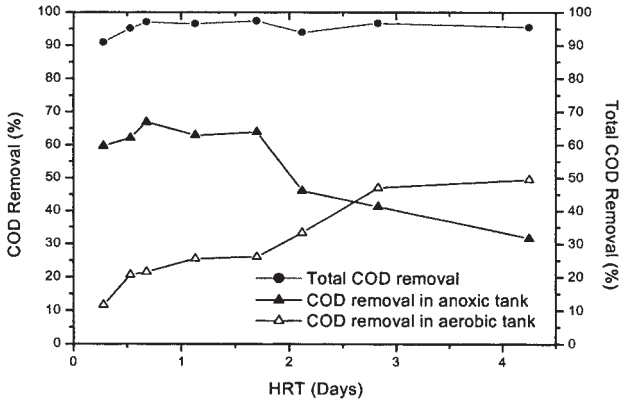

Figure 2. Influence of HRT on COD removal efficiency.

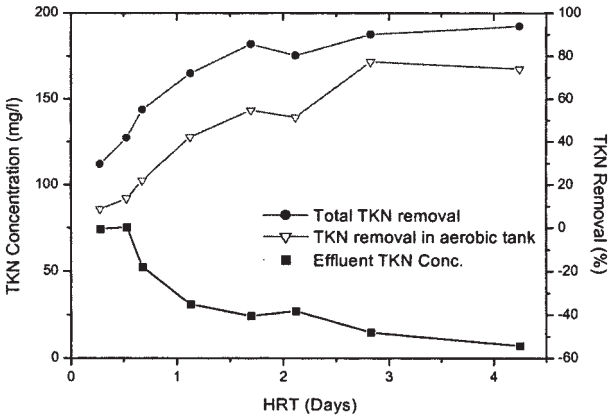

Figure 3. Influence of HRT on TKN removal efficiency.

the total COD removal percentage did not change significantly with decreasing HRT. Moreover, decreasing HRT increased the COD loading in aerobic tank. The presence of high concentrations of heterotrophs induced from high COD loading is the probable reason of nitrification inhibited.[11]

In addition, the ammonia concentration, which is inhibitory to nitrification, increase with increasing TKN loading. Therefore, TKN removal percentage, shown in Fig. 3, decreased of approximately 25% was seen in run 6. As shown in Fig. 4, full nitrification was maintained during runs 1, 2, 3, 4, and 5. In runs 6, 7, and 8, when the TKN loading increased to $0.1\,g\,L^{-1}\,d^{-1}$, a build-up of NH_4-N concentration indicated inhibition of nitrification and/or competition between heterotrophs and autotrophs. The ammonia concentration in effluent increased by approximately 60% and showed a loss of nitrate production. NH_4-N removal percentage also decreased in aerobic tank with decreasing HRT to 1.7 d.

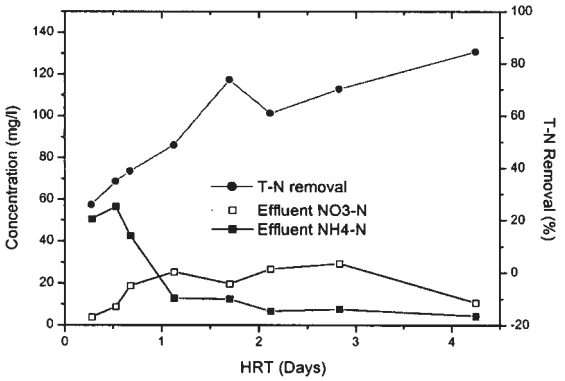

Figure 4. Influence of HRT on T-N removal.

Effect of Mixed Liquor Recycled Rate

In runs A, B, C, D, and E, the effluence of mixed liquor recycled rate was shown in Figs. 5, 6, and 7, the following conclusions are drawn:

(a) In runs A, B, and C, increasing mixed liquor recycled rate increased TKN removal efficiency and decreased NO_3-N concentration in the effluent (Fig. 6). Feed COD concentration was diluted by low COD flows of the recycle at low COD/TN ratio conditions, resulted in low COD values at the entrance to anoxic tank. The consequences of this phenomena increased TKN removal percentage due to low C/N values in aerobic tank. Furthermore, nitrate concentration decreased due to an intensive flux of nitrified flow in anoxic tank. With sufficient carbon source in anoxic tank, NO_3-N removal percentage increased with increasing mixed liquor recycled rate.

(b) In runs D and E, with increasing recycle rate to 5Q and 6Q, the HRT decreased to 4 h in anoxic tank. Lack of sufficient retention time for denitrification in anoxic tank, resulted in high C/N values in aerobic tank. The COD removal ability decreased in anoxic tank and increased in aerobic tank (Fig. 5). Competition between heterotrophs and autotrophs in aerobic tank inhibited nitrification and increased ammonia concentration in the effluent (Fig. 7).

CONCLUSION

Based on the results of this study, the following conclusions can be drawn:

1. Before using a biological nitrogen removal process in industrial wastewater, it is important to identify which organic compounds that might inhibit the ability of nitrifying and denitrifying organisms. The inhibition was related to organic nitrogen compounds (TMAH, MEA) and high pH value in opto-electronic industrial wastewater.

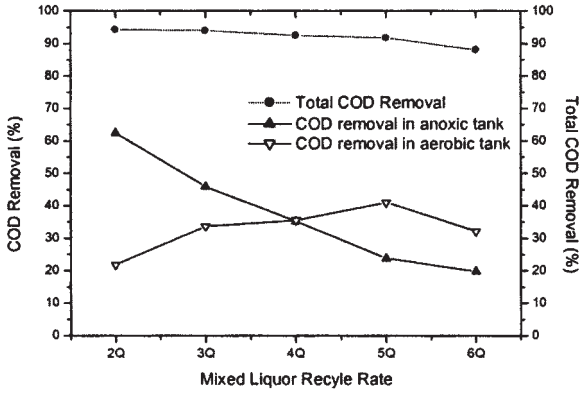

Figure 5. Influence of mixed liquor recycled rate on COD removal.

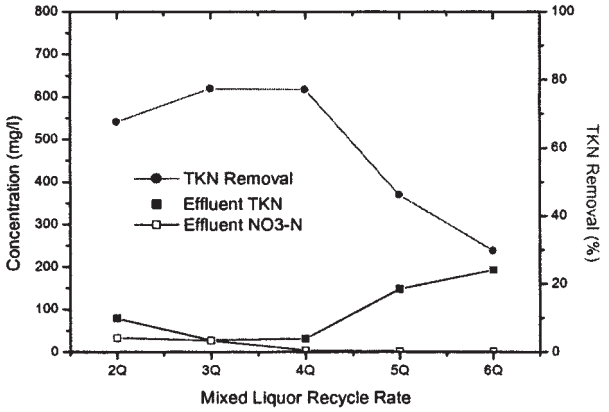

Figure 6. Influence of mixed liquor recycled rate on TKN removal.

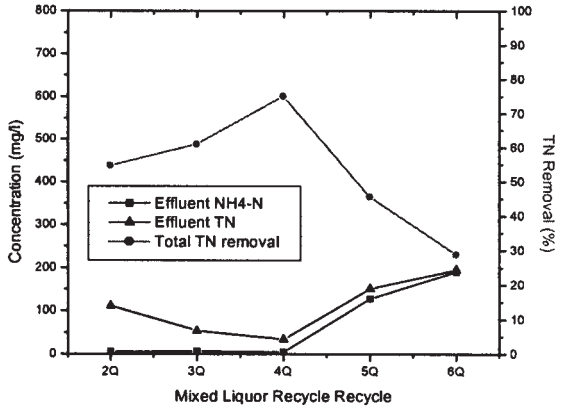

Figure 7. Influence of mixed liquor recycled rate on T-N removal.

2. The anoxic/aerobic pre-denitrification process shows promise as a means of treating opto-electronic industrial wastewater without dilution. Under suitable HRT (1.7 d) and mixed liquor recycled rate (4Q), effluent of NH_4-N, NO_3-N, and COD can fall below 20, 30, and 80 mg/L.
3. For low feed COD/T-N ratio conditions (COD/T-N < 10), increasing mixed liquor recycled rate to 5Q may distort the carbon/nitrate ratio which is essential for complete denitrification. Moreover, uncompleted denitrification resulted in high C/N values in aerobic tank. Accumulation of ammonia in aerobic tank inhibited nitrification and decreased TN removal percentage.
4. The mixed liquor recycled rate, in general, has an optimum value that results in complete denitrification and minimum level of nitrogen in the effluent. In this study, the optimum value of mixed liquor recycled rate is 4Q. Increasing mixed liquor recycled rate to 5Q or 6Q accumulated ammonia and inhibited nitrification.

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