Journal of Environmental Sciences Vol.11, No.1, pp.93—99, 1999 ISSN 1001—0742

Terephthalic acid wastewater treatment by using two-stage aerobic process

Qi Hui-min, Liu Nian-zeng, Cui Feng

Fushun Research Institute of Petroleum and Petrochemicals, SINOPEC, Fushun, Liaoning 113001, China

Abstract—Based on the tests between anoxic and aerobic process, the two-stage aerobic process with a biological selector was chosen to treat terephthalic acid wastewater (PTA). By adopting the two-stage aerobic process, the COD_{Cr} in PTA wastewater could be reduced from 4000—6000 mg/L to below 100 mg/L; the COD loading in the first aerobic tank could reach 7.0 to 8.0 $kgCOD_{Cr}/(m^3 \cdot d)$ and that of the second stage was from 0.2 to 0.4 $kgCOD_{Cr}/(m^3 \cdot d)$. Further researches on the kinetics of substrate degradation were carried out.

Keywords: PTA wastewater, two-stage aerobic, treatment.

1 Introduction

The terephthalic acid (PTA) wastewater contains terephthalic acid (TA), acetic acid and methyl acetate, and so on (Table 1). PTA wastewater is very difficult to be treated because of its high COD_{Cr}, and is becoming more and more important with more PTA production plants put into operation.

In order to treat PTA wastewater, Amoco Company in USA adopts an extended-aeration process, which may keep COD_{Cr} in the effluent below 100 mg/L, but the hydraulic residence time (HRT) in this process is too long (about 15 days), which means that has to take the large area and investments. Yangzi Petrochemical Company in China adopts an anoxic-aerobic (A/O) process, the results are also unsatisfactory. Even a two-stage A/O system is used, COD_{Cr} in the effluent is still over 150 mg/L.

Based on the tests between the anoxic and aerobic process, it is better to choose the two-stage aerobic (O-O) process with a biological selector to treat PTA wastewater. Using the O-O process, COD_{Cr} in PTA wastewater can be reduced from 4000—6000 mg/L to below 100 mg/L; COD loading in the first aerobic tank could reach 7.0 to 8.0 $kgCOD_{Cr}/(m^3 \cdot d)$, and that of the second was from 0.2 to 0.4 kg $COD_{Cr}/(m^3 \cdot d)$. Furthermore, kinetics of substrate degradation has been studied and the related kinetic coefficients have been determined.

2 Process selection

2.1 PTA wastewater

The quality of PTA wastewater for testing was provided by ICI Corporation of England and PTA production plants in China (Table 1).

2.2 Batch tests

The purposes of aerobic and anoxic batch tests are to choose a process for treating PTA wastewater. Because the anaerobic plant for treating PTA wastewater at Yangzi Petrochemical Company has worked unsteadily, and COD or TA removal efficiency is very low, the anaerobic batch test is not be considered here. The temperature in anoxic or aerobic reaction tank was 20—30℃. In the anoxic tank, initial COD_{Cr} was 2700 mg/L, the mixed liquor suspended solid

(MLSS) was 7.8 g/L; and dissolved oxygen was kept in the range of 0—0.5 mg/L. The COD_{Cr}, MLSS and dissolved oxygen in the aerobic tank were 2800 mg/L, 7.5 g/L and 1.0—2.0 mg/L, respectively. The results of two tests are shown in Fig.1 and Fig. 2.

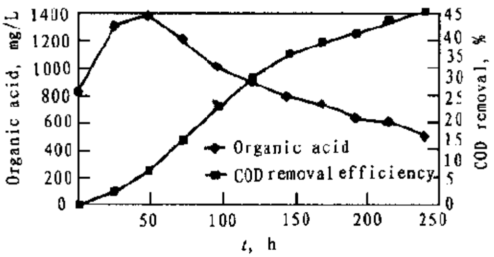

Fig.1 The batch test of anoxic

Table 1 Quality of wastewater

Item	Range
COD_{Cr}, mg/L	4000—5000
BOD_5, mg/L	2600—3800
Terephthalic acid, mg/L	800—1200
Acetic acid, mg/L	800 1200
Methyl acetate, mg/L	500—800
pH	3.5—4.5

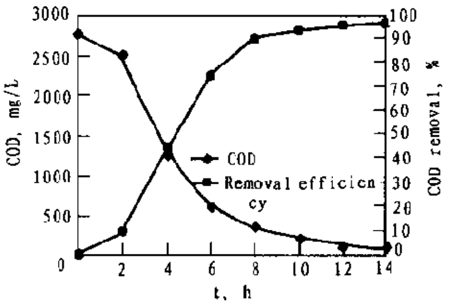

Fig.2 The batch test of aerobic

The anoxic batch test (Fig. 1) showed that degradation of substrate was slow and COD_{Cr} removal efficiency was only about 45 percent after 250 hours. But volatile acid concentration increase by 42% in 48 hours (mainly because a part of the TA was hydrolyzed into acetic acid), which could improve the biodegrade ability of the PTA wastewater.

In the aerobic test (Fig.2), the degradation of substrate was very quick, the COD_{Cr} removal efficiency reached 95 percent after 13 hours (the COD_{Cr} was reduced from 2800 mg/L to below 100 mg/L). The results of batch aerobic test also showed that COD_{Cr} removal had dropped apparently after about 85 percent COD_{Cr} was reduced. Therefore, the aerobic process should be chosen to treat PTA wastewater. Considering that COD removal in the aerobic test became slowly after removal of 85% COD_{Cr}, the aerobic process may be divided into two stages to improve COD_{Cr} removal efficiency. One stage operates at high loading and the other at low. Furthermore, considering the anoxic-aerobic (A/O) system has the advantages of controlling sludge bulking and reducing excess sludge, the anoxic process may be used as a pretreatment stage in the aerobic process of PTA wastewater. That is, treating process may include anoxic stage and two aerobic stages (A-O-O) together for treatment of PTA wastewater.

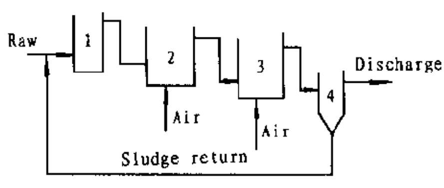

Fig.3 The flow chart of A-O-O process with single sludge return
1. anoxic tank; 2. first aerobic tank;
3. second aerobic tank; 4. setting tank

2.3 Tests of A-O-O process

2.3.1 Process of A-O-O with single sludge return

The A-O-O process with single sludge return includes one anoxic tank, first stage aerobic tank, second aerobic tank and a settling tank; the sludge is returned to the inlet of the anoxic tank from the settling tank (Fig.3).

The volumes of the anoxic tank, first aerobic tank and second aerobic tank were 12.6, 25.6 and 25.6 liter (L) respectively. The total HRT was 5.31 days (anoxic tank was 1.05 days and aerobic tanks were 2.13 days respectively), the average COD_{Cr} was 5000 mg/L, the average BOD_5 was 3300 mg/L. The sludge recirculation ratio was 1.0—1.5, the temperature was 20—30℃; the MLSS in anoxic tank and aerobic tanks were 5—6 g/L. Because the COD removal efficiency was very low in anoxic tank, the sodium organic acid may not degraded into sodium carbonate (or sodium bicarbonate) which can increase the pH of wastewater. In order to make anoxic tank operate normally, alkali must be added to wastewater by about 1g per liter wastewater so that pH is adjusted to 5.0—5.5. The result of the A-O-O processes is shown in Fig.4.

During the experiment, we found the COD_{Cr} removal efficiency of anoxic tank was below 10%. Fig.4 shows: the effluent COD_{Cr} of second aerobic tank sometimes is higher than that of first aerobic tank. This phenomenon was caused by following reason: (1) analysis error; (2) because the COD_{Cr} removal efficiency of second aerobic tank was low, the COD fluctuation of the influent may also cause this phenomenon. It had been found that microbial community structure of second stage is similar to that of first stage, which is one of the factors resulting in low COD removal efficiency of second stage. In order to increase the COD removal efficiency of second aerobic tank and keep the effluent COD_{Cr} below 100 mg/L, the sludge from first stage and second stage should return to their inlets respectively.

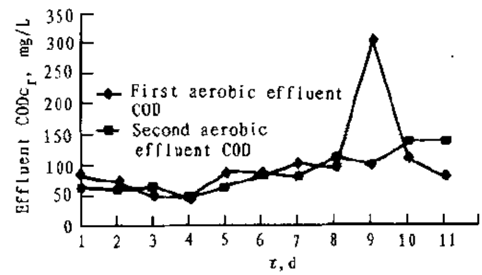

Fig.4 The results of A-O-O process with single sludge return

2.3.2 A-O-O process with individual sludge return

The flow chart of A-O-O process with individual sludge return is shown in Fig.5. It has two settling tanks to make the sludge return separately. The operation conditions were the same to that of A-O-O process with single sludge return. The recirculation ratios of first stage and second stage were 1.0—1.5. The experimental results are shown in Fig.6.

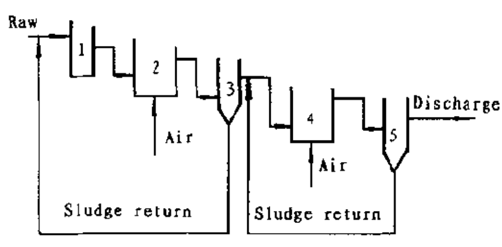

Fig.5 The flow sheet of the A-O-O process with individual reflux
1. anoxic tank; 2. first aerobic tank;
3. first setting tank; 4. second aerobic tank;
5. second setting tank

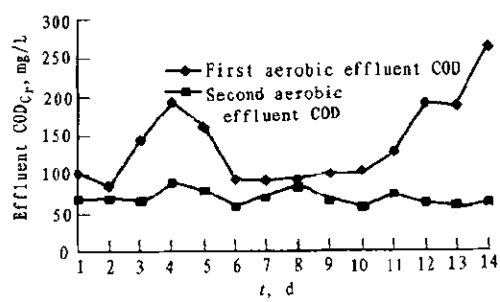

Fig.6 The results of A-O-O process with an individual sludge return

Compared Fig.6 with Fig.4, it is evident that the COD removal efficiency of second aerobic tank was improved after adopting individual sludge return.

2.4 Tests of O-O process

According above results of test, the O-O process perhaps is a good choice. Considering that a high concentration of organic acid will stimulate the growth of filamentous bacteria in activated sludge, some measures must be taken to improve the settle ability of activated sludge. A biological selector, which is placed before aerobic tank, is one of measures. In fact, a selector is a little aerobic tank with HRT of only 10 to 40 minutes. The COD concentration in selector is comparatively high, which has positive effect on growth of flocculate bacteria and inhibits growth of filamentous bacteria. The flow sheet of the O-O process with biological selector is shown in Fig.7.

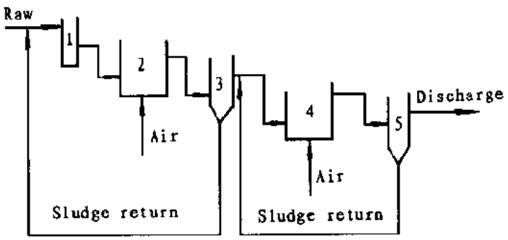

Fig.7 The flow sheet of the O-O process with biological selector
1. biological selector; 2. first aerobic tank;
3. first setting tank; 4: second aerobic tank;
5. second setting tank

In Fig. 7, the volume of the biological selector was 0.3 liter, the HRT was 36 min, and pH of feeds was in range of 3.5 and 4.0, and the total HRT was 4.26 days (first and second aerobic were 2.13 days respectively). The other operating condition was the same to the A-O-O process with individual sludge return. The results are showed in Fig. 8. Compared Fig.8 with Fig.6, the effluent COD of the O-O process and that of A-O-O process are basically the same. Because the HRT of the O-O process is lower than the A-O-O process, so the COD loading of O-O process is higher than that of the A-O-O process. The contrast test of COD loading capacity between the A-O-O process and the O-O process was carried out.

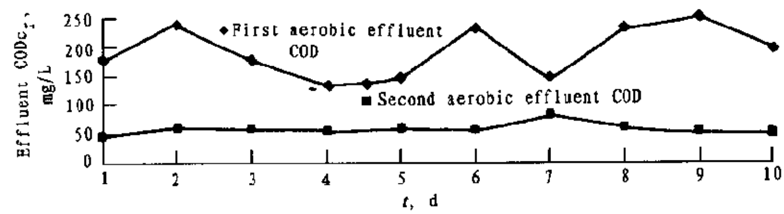

Fig.8 The results of the O-O process with a biological selector

3 Comparison tests between the A-O-O process and the O-O process

In the contrast testes, the A-O-O process and O-O process both were tested with individual sludge return. The volume of anoxic tank was 12.6L, and that of the biological selector was 0.3L. The COD loading increased gradually from about 1 $kgCOD_{Cr}/(m^3 \cdot d)$. The other conditions were the same to the above. The results are shown in Fig.9 and Fig.10.

Comparing the results of A-O-O process and O-O process, the effluent COD by A-O-O process

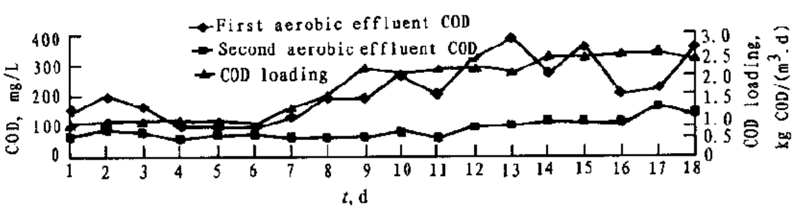

Fig.9 The results of comparison test by A-O-O process

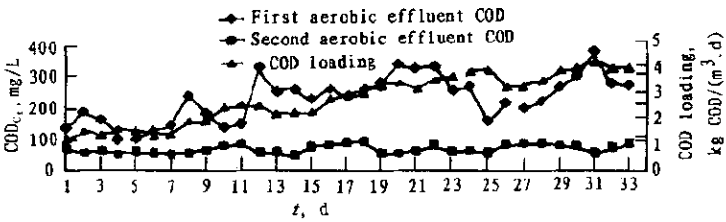

Fig.10 The results of comparison by O-O process with biological selector

reached over 100 mg/L when COD loading reached about 2.3kgCOD_{Cr}/($m^3 \cdot d$) (The HRT was 2.3 days), and that by O-O process with a biological selector was below 100 mg/L even the COD loading reached 4.0 kgCOD_{Cr}/($m^3 \cdot d$) (the COD loading of first aerobic tank reached 8.0 kg COD_{Cr}/($m^3 \cdot d$) and the HRT was only 1.07 days). During the O-O process experiments, it was noticed that the active sludge has an excellent settling characteristics, and sludge volume index (SVI) was below 100, perhaps the reason is that the selector plays an important role.

The O-O process has a higher COD removal efficiency and COD loading capacity. In addition, the reagent consumption in the O-O process is lower than that of the A-O-O process. Because the COD removal efficiency of first aerobic tank can reach 90 percent, and most of sodium organic acid can be degraded into Na_2CO_3($NaHCO_3$), CO_2 and H_2O, which can increase pH of the mixed liquor to 7.8—8.0 (when the pH of feeds was 3.5—4.0). It was obvious that the O-O process is more suitable to treat PTA wastewater.

4 Kinetics of substrate degradation of PTA wastewater

4.1 Kinetics of substrate degradation in first aerobic tank

At steady situation, a mass balance for first aerobic tank is shown in Fig.11.

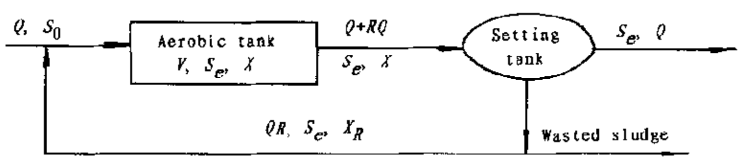

Fig.11 The balance sheet of aerobic tank

In Fig.11, S_o is the influent COD_{Cr} concentration, g/L; S_e is the effluent COD_{Cr} concentration, g/L; X is the concentration of activated sludge in reactor, g/L; R is the recirculation ratio of sludge; V is the volume of reactor, L; Q is the influent flowrate, L/d; X_R is the concentration of returned sludge.

That is

$$S_oQ + S_eRQ - (Q + RQ)S_e + V\frac{dS}{dt} = 0, \tag{1}$$

$$-\frac{dS}{dt} = \frac{Q(S_o - S_e)}{V}. \tag{2}$$

At steady state, Monod Equation can be written as:

$$-\frac{dS}{dt} = \frac{q_{max} X S_e}{K_s + S_e}, \tag{3}$$

where q_{max} is the maximum rate of substrate degradation; K_s is the half velocity constant, g/L.

In Equation (2), $-\frac{dS}{dt}$ is replaced by Equation (3), then

$$\frac{XV}{Q(S_o - S_e)} = \frac{K_s}{q_{max} S_e} + \frac{1}{q_{max}}. \tag{4}$$

Based on four sets of feeds with different COD concentrations, the kinetic experiments accomplished. The average values of 7 days are listed in Table 2.

Table 2 Experimental data and determination of the kinetic coefficients of first aerobic tank

Parameters	Test number			
	No.1	No.2	No.3	No.4
V, L	25.6	25.6	25.6	25.6
S_o, g/L	4.721	4.873	5.378	6.847
S_e, g/L	0.129	0.181	0.253	0.345
X, g/L	5.7	5.2	6.2	6.3
Q, L/d	17.1	17.7	26.4	22.2

Using linear regression method, we obtain:

$$\frac{XV}{Q(S_o - S_e)} = 0.16 \frac{1}{S_e} + 0.62. \tag{5}$$

It means:

$$q_{max} = 1.61/\text{d}, \ K_s = 0.25 \text{ g/L}.$$

4.2 Kinetics of substrate degradation of second aerobic tank

The experimental data of second aerobic tank are shown in Table 3.

Table 3 Experimental data and determination of the kinetic coefficients of second aerobic tank

Parameters	Test number			
	No.1	No.2	No.3	No.4
V, L	18.5	18.5	18.5	18.5
S_o, g/L	0.462	0.332	0.317	0.250
S_e, g/L	0.137	0.079	0.067	0.051
X, g/L	3.1	2.7	3.1	2.7
Q, L/d	22.6	22.3	22.7	22.0

Using linear regression method, we obtain:

$$\frac{XV}{Q(S_o - S_e)} = 0.3 \frac{1}{S_e} + 5.4 . \tag{6}$$

It means:

$$q_{max} = 0.18/\text{d}, \ K_s = 0.054 \text{ g/L}.$$

5 Application of the O-O process in commercial plant

The O-O process containing a selector and individual sludge return has been applied for PTA wastewater treatment since 1994 at Urumchi Petrochemical Factory. The results are as follows

(Table 4).

Table 4 Application of the O-O process at Urumchi Petrochemical Factory

	pH		COD, mg/L		Loading
	Influent	Effluent	Influent	Effluent	kgCOD/(m^3·d)
Biological selector	4.0±0.5	7.8±0.5	4173±639	2073±236	
Primary tank	7.8±0.5	8.4±0.6	2073±236	239±78	2.5±1.0
Secondary tank	8.4±0.6	8.8±0.6	239±78	74±14	0.2±0.2

6 Conclusions

According to the experimental results, the O-O process is a better choice for treating PTA wastewater.

Adopting the O-O process to treat PTA wastewater, the COD could be reduced from 4000—6000 mg/L to below 100 mg/L, the total COD loading could reach 4 kg COD/(m^3·d), and that of first aerobic tank and second aerobic tank could reach 8.0 kg COD/(m^3·d) and 0.2—0.4 kg COD/(m^3·d), respectively.

Using the O-O process for the treatment of PTA wastewater, the kinetics of substrate degradation in first aerobic tank as:

$$\frac{XV}{Q(S_o - S_e)} = 0.16\frac{1}{S_e} + 0.62$$

and $q_{max} = 1.61/d$, $K_s = 0.25$ g/L.

The kinetics of substrate degradation in second aerobic tank as:

$$\frac{XV}{Q(S_o - S_e)} = 0.3\frac{1}{S_e} + 5.4$$

and $q_{max} = 0.18/d$, $K_s = 0.054$ g/L.

It is not necessary to add NaOH to adjust the pH of wastewater, if its pH is 3.5—4.5.

References

Chuduba P, Pujol R, 1994. Wat Sci Tech, 29(7):177—180

Glen T, Daigger Millard Robins Jr, 1985. Journal WPCF, 57(3):220—226

(Received for review February 19, 1998. Accepted May 29, 1998)