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## A two-stage anaerobic system for biodegrading wastewater containing terephthalic acid and high strength easily degradable pollutants

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**Abstract:** The high strength easily biodegradable pollutants (represented by  $COD_E$ ) are strong inhibitors of terephthalic acid (TA) anaerobic biodegradation. At the same time, TA can inhibit easily biodegradable pollutants removal under anaerobic conditions to a limited extent. This mutual inhibition could happen and cause a low removal efficiency of both TA and  $COD_E$ , when the effluent from TA workshops containing TA and easily biodegradable pollutants are treated by a single anaerobic reactor system. Based upon the treatment kinetics analysis of both TA degradation and  $COD_E$  removal, a two-stage up-flow anaerobic sludge blanket and up-flow fixed film reactor (UASB-UAFF) system for dealing with this kind of wastewater was developed and run successfully at laboratory scale. An UASB reactor with the methanogenic consortium as the first stage removes the easily biodegradable pollutants ( $COD_E$ ). An UAFF reactor as the second stage is mainly in charge of TA degradation. At a  $COD_E$  loading of 15.3 g/(L·d) and a TA loading of 1.4 g/(L·d), HRT 18.5h, the  $COD_E$  and TA removal rate of the system reached 89.2% and 71.6%, respectively.

**Keywords:** wastewater treatment; anaerobic system; kinetics; terephthalic acid (TA); inhibition

### Introduction

Terephthalic acid (TA) is one of the raw materials widely used in the petrochemical synthesis industry such as resin, terylene fibre, plastic film and dye and so on. In 1999, the total output of TA was about 100 billion ton per year, and countries or areas producing TA include USA, Japan, South Korea, EEC, China, Mexico, Brazil, and Columbia. With the increasing of the TA production, there is great concern for contamination of TA derived from TA workshop effluent since TA was considered as a potential hazardous pollutant (Liu, 1990; Pang, 1994).

TA-containing wastewater usually can be treated by aerobic or anaerobic technology. An activated sludge technology was reportedly used for this kind of wastewater treatment (He, 1991). At HRT 3—5 days, COD concentration 10000 mg/L, TA concentration 1000 mg/L, COD and TA removal rate could reach 90% and 80%, respectively. Although TA and COD can be removed efficiently by the aerobic technology, the process takes a long time and consumes large amounts of energy. In order to shorten the process duration and to reduce the energy consumption as well as the high cost for disposing the large amount of excess sludge produced by aerobic treatment, lots of efforts have been reported with the focus on adopting a one stage anaerobic process under methane fermentation mode, or an anaerobic-aerobic in series process, instead of the traditionally used aerobic one, but the TA removal rates reported were no more than 40%. Previous research works were mainly concentrated on how to maintain high concentration of biomass in anaerobic reactor and determination of the suitable condition for TA-containing wastewater treatment. Xin *et al.* (Xin, 1991) used a hybrid anaerobic reactor at laboratory scale for TA-containing wastewater treatment, at HRT 14h, COD concentration 4000 mg/L, TA concentration 1200 mg/L. COD and TA removals reached 76.4% and 38.2%, respectively. Macarie *et al.* (Macarie, 1992) obtained a result of COD removal rate 74.5%, TA removal rate 37.6% at COD loading 1.89 g/(L·d), HRT 77h, by using a tubular fixed film reactor. Research works conducted in a single UASB reactor (Li, 1995) previously showed that at HRT 18h, COD 1000 mg/L, TA 910 mg/L, COD and TA removal rate reached 75.2% and 40.1%. Li *et al.* (Li, 1995) reported that COD and TA removal rate could reach 75% and 40%,

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respectively, in a pilot scale UASB reactor at COD concentration  $7500 \pm 500$  mg/L, TA concentration  $700 \pm 100$  mg/L, HRT 36—48h. These TA degradation rates obviously cannot meet the demand of TA removal and will cause contamination.

Typical data of the effluents from big TA producer's workshops both in China and abroad contained the following concentration of pollutants (in mg/L): TA  $2590 \pm 80$ , easily biodegradable  $\text{CH}_3\text{COOH}$   $1500 \pm 500$ , nearly the same amount of  $\text{CH}_3\text{COOCH}_3$ , total COD 9000—13000. A previous study by Li (Li, 1995) indicated that the existence of 800 mg/L acetic acid can result in a decrease of 57% of TA removal rate under methane fermentation conditions. Moreover, the fact of preferential substrate utilization results in a sequence of attack, and typically those compounds yielding the fastest growth rate will be degraded first (Daniel, 1979; Avin, 1988). For example, methyl acetate may be hydrolyzed into acetic acid and methanol by fermentative bacteria within the methanogenic consortium prior to TA degradation, which will make the inhibition worse. On the other hand, TA inhibits the activity of methanogenic bacteria (Li, 1995) and slows down the process of transforming acetic acid to methane. This is likely the main reason leading to a lower efficiency of the TA biodegradation than that expected in one reactor. The present study aims at dynamically analyzing those rate-limiting factors as well as their cooperative effect on both TA degradation and easily degradable pollutants removal, and explores the feasibility of enhancing TA degradation rate as well as  $\text{COD}_E$  removal rate and improving the treatment process through reducing the mutual inhibition by developing a two-stage anaerobic UASB-UAFF system for this kind of wastewater.

## 1 Materials and methods

Composed water contained the following per liter of water:  $\text{MgSO}_4$  0.2g,  $\text{KH}_2\text{PO}_4$  0.7g,  $\text{NH}_4\text{Cl}$  0.5g,  $\text{Na}_2\text{S}$  0.5g, trace elements solution 5.0 ml. In the composed water, the concentration and kind of carbon source including TA were indicated separately according to the experiment conducted. TA is AP grade, from Schuchardt Co. Germany.

Seed sludge # 1 used for the experiment of  $\text{COD}_E$  biodegradation dynamics: The granular sludge taken from the methanogenic reactor, Shanghai Soybean Products Manufactory, was acclimated in several 500 ml Erlenmeyer flasks for 45d, flasks were incubated at  $36 \pm 1^\circ\text{C}$ , pH 7.0, under anaerobic condition, with shaking twice daily. TA was determined and the gas volume was collected in a Smith fermentation tube and measured daily. The media for acclimation were replaced through a sampling port every three days by fresh composed water containing TA 600 mg/L, glucose 400 mg/L, and acetic acid 2000 mg/L as carbon source.

Seed sludge # 2 used for the experiment of TA biodegradation dynamics: the flocculent sludge taken from the methanogenic reactor, Wuxi Citric Acid Fermentation Plant, was enriched and acclimated with TA as sole carbon source at  $36 \pm 1^\circ\text{C}$  under nitrate respiration mode in the first three weeks, then transformed in a stepwise manner to methane fermentation status in another three weeks, and totally lasted for three months, which means nitrate was gradually reduced till to zero addition. The media was replaced through a sampling port once a week with fresh composed water, for nitrate respiration mode containing TA 0.5—1.0 g/L,  $\text{KNO}_3$  5.0 g/L,  $\text{MgSO}_4$  0.2 g/L,  $\text{KH}_2\text{PO}_4$  0.2 g/L,  $\text{NH}_4\text{Cl}$  0.5 g/L,  $\text{Na}_2\text{S}$  0.5 g/L and trace elements solution 5.0 ml/L, for methane fermentation mode containing: TA 0.5—1.0 g/L, yeast extract 0—2.0 g/L,  $\text{MgSO}_4$  0.2 g/L,  $\text{KH}_2\text{PO}_4$  0.7 g/L,  $\text{NH}_4\text{Cl}$  0.5 g/L,  $\text{Na}_2\text{S}$  0.5 g/L, trace elements solution 5.0 ml/L.

Dynamics of  $\text{COD}_E$  removal study: The experiment of  $\text{COD}_E$  removal dynamics inhibited by TA was conducted in fed-batch mode in 500 ml round bottom flasks with gas collector in triplicates. The seed sludge # 1 was inoculated to 500 ml composed wastewater with glucose and sodium acetate in a calculated COD ratio of 5.5/L as carbon source, in which the VSS concentration reached 6.686 gVSS/L. TA was added in a stepwise manner and shaken once every two hours, the temperature and pH were kept at  $36 \pm$

1°C, pH 7.0. TA and  $COD_E$  were quantified once every 2–4h, specific rates of TA degradation and  $COD_E$  removal were calculated with initial velocities.

**Dynamics of TA degradation study:** This experiment was carried out in a similar manner as the above, except the quantification of TA and  $COD_E$  were taken once every 10–16h. The seed sludge # 2 was inoculated to the composed water and the VSS reached 7.848 g/L.  $C_{TA}$  (TA conc.) was kept at about  $300 \pm 20$  mg/L, to ensure no inhibition to both the  $q_{COD}$  and  $q_{TA}$  throughout the experiment. The  $C_{COD}$  ( $COD_E$  conc.) was raised in a stepwise manner by adding the acetate-glucose solution in a calculated COD ratio of 5.5/L.

**Start-up of UASB and UAFF reactor:** The UASB reactor was started up with composed water containing acetate, glucose in a ratio of 5.5/1 and a few TA (132 mg/L) as carbon sources, 200 ml well acclimated granular sludge from a methanogenic reactor was inoculated. The composed water was continuously fed in with the initial  $COD_E$  and TA load 2 g/(L·d) and 0.16 g/(L·d). While the  $r_{COD}$  ( $COD_E$  removal rate) reached 80%, both the  $L_{COD-v}$  ( $COD_E$  volumetric loading) and  $L_{TA-v}$  (TA volumetric loading) were raised in stepwise manner, until the  $COD_E$  and TA influent concentration reached 10800 mg/L and 1000 mg/L, respectively. With inoculation of 200 ml well acclimated flocculent sludge, the UAFF reactor was also started up with composed water, in which TA was the main carbon source and the COD (TA):N:P was 200:5:1. The  $L_{TA-v}$  and  $L_{COD-v}$  were raised in stepwise manner on the condition that TA removal rate achieved 60%, until TA influent concentration was increased to 1.3 g/L.

**Experimental apparatus:** The two-stage UASB-UAFF system is shown in Fig. 1, both reactors made of Plexiglas, each with a working volume of 700 ml. The UAFF reactor was packed with 25 mm Pall-ring (Shanghai Plastics, Inc., Shanghai, China).

## 2 Analytical methods

Liquid samples collected daily from both of the batch and continuous reactor were filtrated first, and then the filtrate was used for TA, COD and pH value determination. TA was quantified spectrophotometrically (Spectrophotometer WFZ900-D4, Beijing Analytical Instrument Factory, China), the OD value at 242 nm is proportional to TA concentration with  $r = 0.998$ . All analysis for COD, suspended solids(SS), and mixed liquor volatile suspended solids(MLVSS) were conducted according to standard methods (American Public Health Association, 1985). Concentration of  $COD_E$  specifically represents the content of easily biodegradable organic material. In TA containing wastewater,  $COD_E$  can be calculated by deducting the amount of TA contributed COD, which can be calculated theoretically, from the total  $COD_T$ . Hydrogen and methane gas were analyzed with a gas chromatograph (Shimadzu GC-8AFT, Japan) equipped with a TCD detector, and a GXD104 column, with  $N_2$  as the carrier gas and a flow rate of 25 ml/min. pH was measured with pH meter (pHS-2C, Shanghai Analytical Instrument Plant, China).

## 3 Results and discussion

### 3.1 Mutual inhibition dynamics of $COD_E$ removal and TA degradation

The experimental results of  $COD_E$  removal dynamics inhibited by TA are listed in Table 1. In Table 1,  $q_{COD}$  was calculated according to the  $COD_E$  removal kinetics model without TA inhibition (Eq. (1)) constructed by Li *et al.* (Li, 1995),  $q_{COD-TA}$  in the exp. column was the average value of three parallel test data obtained from  $COD_E$  removal kinetics experiment, and  $q_{COD-TA}$  value in the formula column was

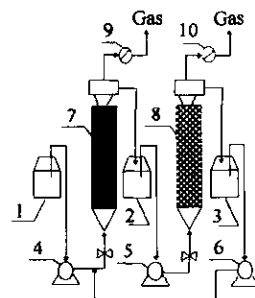


Fig. 1 Schematic chart of UASB-UAFF system

1, 2, 3: influent and effluent bottle; 4, 5, 6: pump; 7: UASB reactor; 8: UAFF reactor; 9, 10: gas flow meter

calculated according to the COD<sub>E</sub> removal kinetics model(Eq.(2)) with TA inhibition (Li, 1995).

$$q_{COD} = \frac{1}{x} \cdot \frac{dS}{dt} = q_{COD-max} \cdot \frac{S}{K_s + S}, \tag{1}$$

where  $q_{COD}$  = specific removal rate of COD<sub>E</sub> without TA being added in the composed water(gCOD/(d·gVSS));  $K_s$  = 3.1718 gCOD/L, substrate constant;  $q_{COD-max}$  = 3.663 gCOD/(d·g VSS), the maximum of specific COD<sub>E</sub> removal rate;  $S$  = COD<sub>E</sub> concentration, mgCOD/L.

$$q_{COD-TA} = q_{COD-max} \frac{S}{K_s + S} \cdot \frac{(K_c/I)^n}{1 + (K_c/I)^n}, \tag{2}$$

where  $Q_{COD-TA}$  = specific removal rate of COD<sub>E</sub> with TA inhibition, gCOD/(d·gVSS);  $K_c$  = 1353.2 mgTA/L, complex inhibition constant;  $n$  = 3.8436, dimensionless constant.

Results listed in Table 1 indicate that with the increase of TA concentration, the inhibition percentage becomes high, and Table 1 also demonstrates that while the  $C_{TA}$  becomes higher than 1451 mg/L, the measured  $q_{COD}$  goes down to 56.37% of the blank test value; and when  $C_{TA}$  is less than 1050 mg/L, the inhibition effect becomes slight, the measured  $q_{COD-TA}$  goes down to about 27.2% of the blank test value, furthermore, at  $C_{TA}$  less than 748 mg/L, the  $q_{COD-TA}$  only is cut down by 9.12% .

**Table 1 Inhibition percentage of biodegradable pollutants (COD<sub>E</sub>) removal rate caused by TA**

$C_{TA}$ , mg/L	$C_{COD}$ , g/L	$q_{COD-TA}$ , Exp.	$q_{COD}$ , gCOD (d·g VSS)		Inhibition percentage, %
			Formula.	without TA	
150	6.12	2.4211	2.4107	2.4112	0.02
315	5.98	2.3525	2.3424	2.3509	0.36
455	6.12	2.3316	2.3759	2.4112	1.46
601	6.08	2.3261	2.3176	2.4177	4.14
748	5.95	2.0563	2.1715	2.3894	9.12
900	5.83	2.0233	1.9693	2.3724	16.99
1050	6.25	1.5796	1.7722	2.430	27.07
1253	5.95	1.3811	1.3784	2.3894	42.31
1451	6.05	1.136	1.0481	2.4023	56.37
1600	6.11	0.8211	0.8362	2.4112	65.32

Notes: Inhibition percentage of biodegradable pollutants (COD<sub>E</sub>) removal rate caused by TA was calculated by following formula:

$$\text{Inhibition percentage} = \frac{q_{COD} - q_{COD-TA}}{q_{COD}} \times 100\%$$

Fig. 2 gives COD<sub>E</sub> removal kinetics model with TA inhibition shown as line and the experimental data shown as dot, from which we can learn that at  $C_{TA}$  exceeding about 800 mg/L, there is a high decrease of COD<sub>E</sub> removal rate. This critical  $C_{TA}$  suggested that COD<sub>E</sub> might be removed efficiently by keeping  $C_{TA}$  less than 800 mg/L.

**3.2 Dynamics of TA degradation inhibited by COD<sub>E</sub>**

TA degradation kinetics model without COD<sub>E</sub> inhibition (Eq. (3)) is shown as a line in Fig.3, and TA degradation kinetics model with COD<sub>E</sub> inhibition (Eq. (4)) in Fig.4 (Li, 2000). The scatter dots both in Fig.3 and in Fig.4 are experimental data for TA degradation kinetics equation construction. Fig. 3 and Fig. 4 indicate that the experimental data can be simulated by the two kinetic equations, and the equations can be used for predicting the TA degradation.

$$q_{TA} = q_{TA-max} \frac{1}{1 + K_s/S + S/K_{i,s}}. \tag{3}$$

Where  $q_{TA}$  = TA specific degradation rate without COD<sub>E</sub> being added in the composed water, mgTA/(d·gVSS);  $q_{TA-max}$  = 1972.0 mgTA/(d·gVSS), the maximum of specific TA degradation;  $S$  = TA concentration, mgTA/L;  $K_s$  = 20.2844 gTA/L, substrate constant;  $K_{i,s}$  = 0.0108 gTA/L, substrate inhibition constant.

$$q_{TA-COD} = q_{TA-max} \frac{S}{S + K_s [1 + (I - 0.86)/K_{i,I}] + S^2/K_{i,s}}. \tag{4}$$

Where  $Q_{TA}$  = TA specific removal rate with COD<sub>E</sub> inhibition, mg TA/(d·g VSS);  $K_{i,I}$  = 2.041 gCOD/L,

inhibition constant.

Table 2 list the results of TA degradation process inhibited by easily biodegradable pollutants COD<sub>E</sub>, in which,  $q_{TA}$  was calculated according to Eq. (3),  $q_{TA-COD}$  in the exp. and formula column were obtained from experiment and Eq. (4), respectively. Inhibition percentage of  $q_{TA-COD}$  in Table 2 states that at  $C_{COD}$  5680mg/L, the measured  $q_{TA}$  went down by 62.2% compared with its blank test value, while the  $C_{COD}$  (COD<sub>E</sub> conc.) > 2240 mg/L, the measured  $q_{TA}$  gets a 33.3% decrease.

Fig. 4 and Table 2 show that TA degradation is seriously inhibited by easily degradable pollutants (COD<sub>E</sub>).

However, if  $C_{COD}$  can be controlled no more than 2240 mg/L,  $q_{TA-COD}$  will remain more than 66.7% of  $q_{TA}$ , which could still ensure a large amount of the TA being removed.

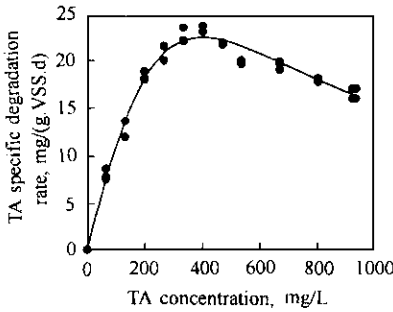


Fig.3 Dynamics of the TA degradation

The dynamics analysis above reveals that the high strength easily biodegradable pollutants(COD<sub>E</sub>) can strongly inhibit TA degradation, and TA can also inhibit COD<sub>E</sub> removal process but to a limited extent. Unfortunately, effluent from TA production workshops is a mixture of TA and easily biodegradable organic materials, which could cause the mutual inhibition when a one-reactor system was employed for treatment of this kind of wastewater, and led to the low removal efficiency of the system. The COD<sub>E</sub> inhibition to TA removal could be attributed to the presence of some short-chain volatile fatty acids (VFAs; Buswell, 1962; Boone, 1984; Li, 1995), which was confirmed by a set of experimental data shown in Fig. 5.

The idea for solving this problem is to remove the easily biodegradable effluent pollutants (COD<sub>E</sub>) first with the enriched and acclimated methane fermentation microbial consortium in an UASB reactor, and

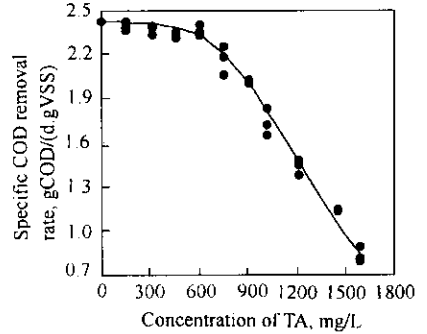


Fig. 2 Dynamics of the COD<sub>E</sub> removal with TA inhibition

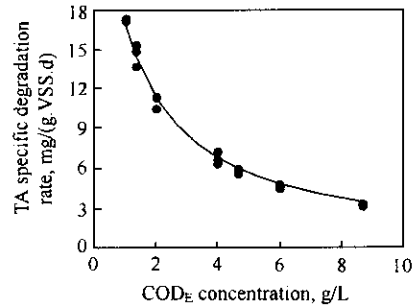


Fig.4 Dynamics of the TA degradation with COD<sub>E</sub> inhibition

Table 2 Inhibition percent of TA degradation caused by biodegradable pollutants COD<sub>E</sub>.

$C_{COD}$ COD <sub>E</sub> conc., mg/L	$C_{TA}$ , TA conc., mg/L	$q_{TA}$ ,		$q_{TA}$ , mgTA/(d·gVSS)	Inhibition percentage, %
		mgTA/(d·gVSS) Exp.	mgTA/(d·gVSS) Formula		
1051	298.9	17.851	18.738	20.448	8.36
1828	270.0	15.011	14.442	19.263	25.02
2236	271.2	12.183	13.056	19.553	33.3
3147	275.1	10.015	10.805	19.693	45.23
4968	317.0	9.15	8.849	20.924	42.289
5681	304.1	7.015	7.788	20.589	62.17
7118	288.0	6.35	6.287	20.121	69.26
9998	263.0	4.11	4.403	19.260	77.46

Notes: Inhibition percentage of TA degradation rate caused by COD<sub>E</sub> was calculated by following formula:  $q_{TA}$  inhibition percentage =  $\frac{q_{TA} - q_{TA-COD}}{q_{TA}} \times 100\%$

which was confirmed by a set of experimental data shown in Fig. 5.

remove TA next with the enriched and acclimated TA reductive cleavage microbial consortium in an UAFF reactor. Because of its unique design, the UASB reactor allows retention of a large concentration of active biomass. As a result, the UASB reactor can operate with a shorter hydraulic retention time (HRT), higher organic loading rate, smaller reactor volume, and less land when compared with other strictly anaerobic reactors. Furthermore, the granular sludge in UASB reactor is highly resistant to poor environment. Due to its obvious advantages, an UASB reactor was adopted as the first step for main removal of easily degradable pollutants ( $COD_E$ ) with TA inhibition to the process. Since anaerobic granular sludge is hard to form with

TA as main carbon source in an UASB reactor (Xin, 1991; Macarie, 1992; Li, 1995a; Li, 1995b), to retain high concentration of anaerobic microorganisms in reactor, a hybrid anaerobic reactor was used by Xin *et al.*, a tubular fixed film reactor was selected by Macarie *et al.*, and a UAF reactor was chosen by Li Gan *et al.* In this study, an UAFF reactor was employed mainly for TA degradation. The average VSS in a large scale UASB reactor reportedly could reach 40 gVSS/L in sludge bed (Pette, 1981), 75 gVSS/L in the fixed filter part of an UAFF (Chen, 1990), the average retained biomass could be 20–30 g/L (van den Berg, 1985). The fact that concentration of VSS in UASB and UAFF reactors at full-scale factory can retain much higher than that in the experimental apparatus suggest that the  $L_{TA-S}$  (mg TA/gVSS) as well as  $L_{COD-S}$  (g COD/gVSS) can be correspondingly cut down under the same effluent flow rate. These lower sludge loadings will obviously be beneficial to the process of both COD removal and TA degradation. In addition, the commonly recognized high resistance of the granular sludge to toxic compounds (Meat, 1987) can help reduce the inhibition effect of TA to  $q_{COD}$  in the UASB reactor to an acceptable low level. If necessary, partially recycling the UAFF effluent to the UASB is a reserve choice. So far, the analysis above gives assurance that the two-stage UASB-UAFF process could be feasible.

### 3.3 Start-up of the UASB-UAFF system

#### 3.3.1 Start-up of UASB and UAFF reactor

To realize this two-stage anaerobic system, the UASB and UAFF reactors were firstly started up respectively. The UASB reactor was started up with acetate, glucose in a ratio of 5.5/1 and a few TA (132 mg/L) as carbon sources in 460 ml-composed water, and with inoculation of 200 ml granular sludge from a methanogenic reactor. The composed water was continuously fed in with the initial  $COD_E$  and TA loading 2 g/(L·d) and 0.16 g/(L·d), i.e. initial  $C_{COD}$  and  $C_{TA}$  were at 1670 mg/L and 132 mg/L, respectively, HRT 20h. While the  $r_{COD}$  ( $COD_E$  removal rate) reached 80%, both the  $L_{COD-V}$  and  $L_{TA-V}$  were raised in stepwise manner, until the TA concentration and  $COD_E$  concentration reached 1000 mg/L<sub>in</sub>, HRT 18.5h, at the end of the 9th week. The start-up process ended when the  $L_{COD-V}$  and  $r_{COD}$  went up to 14 gCOD/(L·d) (i.e.  $C_{COD}$  10800 mg/L, HRT 18.5h) and 80%, respectively, within 70 days as shown in Fig.6.

The UAFF reactor was inoculated with 200 ml well acclimated flocculent sludge and was started up with composed water, in which TA was the main carbon source and the  $COD(TA):N:P$  was 200:5:1. The  $L_{TA-V}$  and  $L_{COD-V}$  were raised also in stepwise manner on the condition that TA removal rate achieved 60%. Until TA influent concentration was increased to 1.08 g/L, i.e. TA loading 1.4 g/(L·d), the start-up process was considered to be finished as shown in Fig.7.

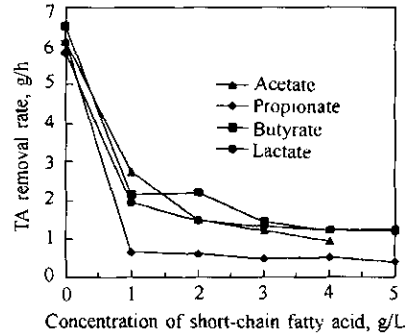


Fig. 5 Effects of short-chain fatty acids on TA degradation

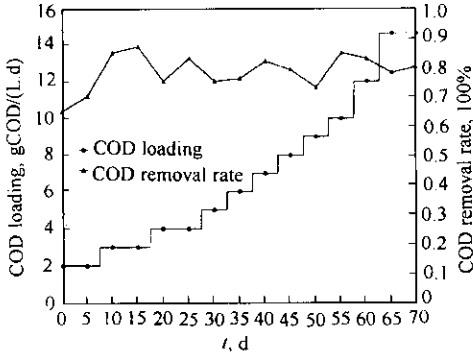


Fig. 6  $COD_E$  loading and removal rate during UASB reactor start-up

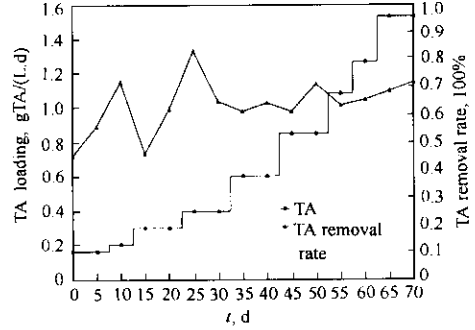


Fig. 7 TA loading and removal rate during UAFF reactor start-up

### 3.3.2 Start-up of the UASB-UAFF process

The two reactors were connected in sequence from UASB to UAFF, which formed the two-stage anaerobic system shown in Fig.1 for TA containing wastewater treatment. The composed wastewater in turn went through from UASB to UAFF. However, to retain the less shock to this system, the inlet concentrations of TA and  $COD_E$  were all set lower than that at the end of starting up of UAFF and UASB, and then raised in the way similar to the single reactor starting up. The processes shown in Fig.8 and Fig. 9 last about 21 days for the system reactors to reach the same degradability as the single reactors. At the end of the start-up process, at HRT 18.5h,  $C_{COD}$  and  $C_{TA}$  in the influent of the system reached 11800 mgCOD/L and 1080 mgTA/L, in the effluent of the UASB reactor, i.e., the influent of the UAFF reactor,  $C_{COD}$  and  $C_{TA}$  were 1770 mgCOD/L and 1080 mgTA/L, and in the effluent of the whole system  $C_{COD}$  and  $C_{TA}$  were 890 mgCOD/L and 307mg/L. The key point for the system start-up and running is to keep a proper concentration of TA and  $COD_E$  in the influent, which, if necessary, can be done by partially recycling the effluent of the UAFF, so that the mutual inhibition between TA degradation and  $COD_E$  removal can be controlled. Finally,  $COD_E$  and TA removal rate of the UASB-UAFF system achieved 89.2% and 71.6%, respectively, at a  $COD_E$  loading of 15.3 g/(L·d), and a TA loading of 1.4 g/(L·d), HRT 18.5h.

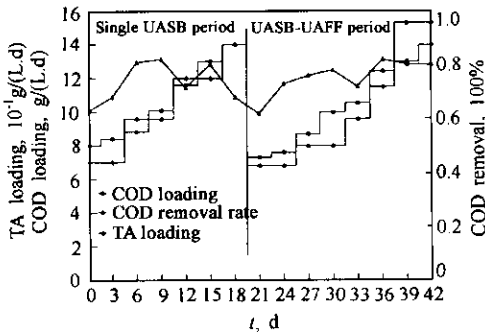


Fig. 8  $COD_E$  loading and removal rate in UASB

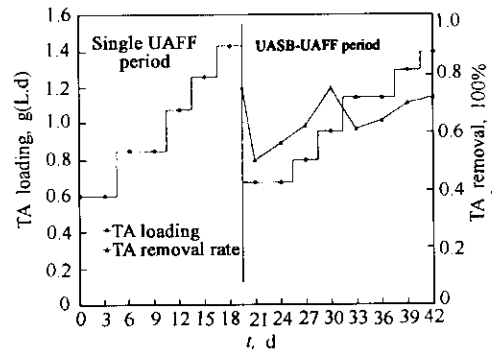


Fig. 9 TA loading and degradation rate in UAFF reactor during start-up of UASB-UAFF system reactor during start-up of the UASB-UAFF system

## 4 Conclusions

Analysis of the kinetics of both TA degradation and  $COD_E$  removal revealed that TA degradation can

be inhibited by easily degradable pollutants, and at the same time TA inhibits removal of easily degradable pollutants. At  $C_{\text{COD}} 5680 \text{ mg/L}$ , the  $q_{\text{TA-COD}}$  decreased by 62.2% compared with the blank test, at  $C_{\text{TA}}$  higher than 1451mg/TA, the  $q_{\text{COD-TA}}$  decreased by 56.37%. This mutual inhibition could lead to lower removal efficiency in single reactor system, which has been demonstrated by previous studies(Xin, 1991; Macarie, 1992; Li, 1995a; Li, 1995b). However, when  $C_{\text{TA}}$  is less than 1050 mg/L, the  $q_{\text{COD-TA}}$  becomes less than 27.2% decrease of  $q_{\text{COD}}$ , and when  $C_{\text{COD}}$  less than 2240 mg/L, remains more than 66.7% of  $q_{\text{TA}}$ , which make it possible that easily degradable pollutants ( $\text{COD}_E$ ) and TA be treated at different stage, when the concentration of TA and  $\text{COD}_E$  in the influent were controlled properly.

On the basis of this viewpoint, a two-stage anaerobic UASB-UAFF system for the treatment of high strength organic wastewater containing TA was started-up and finally performed well at laboratory scale, with easily biodegradable  $\text{COD}_E$  removed first by the methanogenic consortium in an UASB reactor and followed by TA removal in a UAFF reactor containing TA reductive cleavage microbial consortium.  $\text{COD}_E$  and TA removal rate of the system reached 89.2% and 71.6%, respectively, at a  $\text{COD}_E$  loading of 15.3 g/(L·d) and a TA loading of 1.4 g/(L·d), HRT 18.5h.

The founding of present study suggests that not only TA-containing wastewater but also the other wastewater containing a toxic, slowly degradable substrate and readily degradable substrates could be treated by a two-stage anaerobic technology, which might lessen the mutual negative effect on the removal of these two kind of substrates and enhance the treatment efficiency, when proper conditions were controlled.

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