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Biodegradability of terephthalic acid in terylene artificial silk printing and dyeing wastewater

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Abstract: As the characteristic pollutant, terephthalic acid(TA) was in charge of 40%—78% of the total COD of terylene artificial silk printing and dyeing wastewater(TPW-water). The studies on biodegradability of TA were conducted in a serial of activated sludge reactors with TPW-water. TA appeared to be readily biodegradable with removal efficiency over 96.5% under aerobic conditions, hardly biodegradable with removal efficiency below 10% under anoxic conditions and slowly biodegradable with a turnover between 31.4% and 56.0% under anaerobic conditions. TA also accounted for the majority of BOD in TPW-water. The process combined by anoxic, anaerobic and aerobic activated sludge reactor was suitable for TA degradation and TPW-water treatment. Further, the aerobic process was essentially much more effective than the anaerobic or anoxic one to degrade TA in TPW-water.

Keywords: terephthalic acid; biodegradability; bio-treatment; printing and dyeing wastewater; terylene artificial silk

Introduction

In order to get pliable and elegant terylene fabric just like silk, terylene greige cloth has to be pretreated with alkali-decomposing process, that is, terylene greige cloth is hydrolyzed to some extent in NaOH solution at certain temperature and pressure. During this process, superficial terylene fibre is peeled off from the cloth and dissolved into solution, which is discharged as wastewater. Then, the terylene fabric with silken wrinkle and soft feeling is gained, which is called artificial silk fabric. The alkali-decomposing of terylene can be described by the chemical equation as follows:

$$H[-OOC-Ar-COO-CH_2CH_2-]_nOH + NaOH \longrightarrow Na[-OOC-Ar-COO-CH_2CH_2-]_mOH + (Na-OOC-Ar-COO-Na) + (HO-CH_2CH_2-OH) \qquad n > m.$$

Based on the chemical equation, it is believed that terephthalic acid(TA) and ethylene glycol are the main pollutants in the wastewater from this process. The chemical oxygen demand (COD) of the wastewater approved to be ten thousands milligram per liter.

The wastewater from alkali-decomposing process mixed with those from printing, dyeing, potch and other processes is named terylene artificial silk printing and dyeing wastewater (TPW-water). In fact, the wastewater from alkali-decomposing process only accounts for less than 15% of the total amount of TPW-water, but the equivalent COD from TA shares about half of total COD of TPW-water. Evidently, TA is the characteristic pollutant of the wastewater.

As a new kind of textile industrial wastewater, TPW-water is different from traditional printing and dyeing wastewater. The biodegradability of TA plays a very important role in TPW-water bio-treatment due to its high concentration.

It has been noted that microorganisms used to degrade TA exist in soil and manure (Ribbons, 1960), aquatic sediment (Aftring, 1981) and activated sludge from wastewater treatment facilities(Lin, 1986). In aqueous solution, TA is readily degradable under aerobic conditions and more difficult to be degraded under anaerobic conditions in laboratory scale (Tong, 1990; Wan, 1990). However, the degradability of TA varies distinctly when industrial wastewater containing TA is dealt with. For an example, the removal efficiency of TA(η_{TA}) is only 25.6% in chemical industrial wastewater(Bao, 1985) but high than 86% in the effluent of pure terephthalic acid factory(Zhao, 1994) during bio-treatment under aerobic conditions. Thus, the degradability of TA should be tested according to actual conditions while industrial wastewater is considered.

In spite of the well-ground research in TA degradation by microorganisms in aqueous solution, the degradability of TA in TPW-water has not been well understood yet. Usually, the low efficiency of TPW-water bio-treatment is attributed to the difficulty of TA degradation, and TA has to be separated from the wastewater of alkali-decomposing process by adjusting pH below 5.0 before biological process is used for TPW-water treatment(Wang, 1998; Ma, 1999).

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For the sake of selecting reasonable process for TPW-water treatment, it is necessary to have a clear view on the TA degradation. In this paper, the degradability of TA in TPW-water is discussed, focusing on the removal efficiency of TA under aerobic, anoxic or anaerobic conditions.

1 Material and methods

1.1 Wastewater

TPW-water concerned in this paper came from the center pump station for TPW-water in Shaoxing County, China. In Table 1 a survey is given of main pollutants in TPW-water from September, 1999 to September, 2000. By actual test, 1.0 g TA in TPW-water is equivalent to 1.39 g COD, that is, TA shares 40%—78% of total COD of TPW-water.

1.2 Experimental procedures

Fig.1 illustrates the set up of biological process, which has been optimized for TPW-water treatment in a laboratory scale. The aerobic process shown in part Ⅴ, the anoxic process shown in part Ⅱ and expanded granular sludge bed(EGSB) process shown in part Ⅳ was introduced in turn. Finally, combined biological process, in which anoxic, anaerobic and aerobic activated sludge reactors were connected in series with sludge setting and reflux units respectively and a neutralization unit(part Ⅲ), was applied to study the effectiveness of bio-treatment.

Table 2 gives the operational factors optimized in the first stage of the experiment. The aeration tank reactor (ATR) was operated at temperature(T) 30℃, influent pH ≤ 11.0, mixed liquor suspended solid (MLSS) 2.5—3.5 g/L and dissolved oxygen (DO) 3.0—5.5 mg/L with bubbling at a ratio of air to wastewater(A/W) 15—20 Nm^3/m^3. The continuous stirred tank reactor (CSTR) mixed at 60 r/min was employed to deal with the anoxic treatment at T 30℃, influent pH ≤ 11.0, MLSS 3.6—4.2 g/L without air supply. The EGSB was conducted at influent pH 6.8—7.5 and up-flow linear velocity 3—5 m/h, with sludge volume index (SVI) 22 in bed. The temperature was controlled at 33℃.

Table 1 TPW-water quality

Indexes	pH	COD, mg/L	BOD, mg/L	TA, mg/L	COL, unit
Range	8.24—12.78	780—3116	325—1436	286—1279	250—600
Average	—	1780	703	710	—

The combined process was operated at a flow-rate about 7.5 L/d and HRT 2.5 d, which was divided into 15 h in CSTR, 32 h in EGSB, 12 h in ATR and 1 h in neutralization reactor.

In order to value the influence of TPW-water variation on the biodegradability of TA, the experiment lasted one year at the center pump station for TPW-water, Shaoxing County.

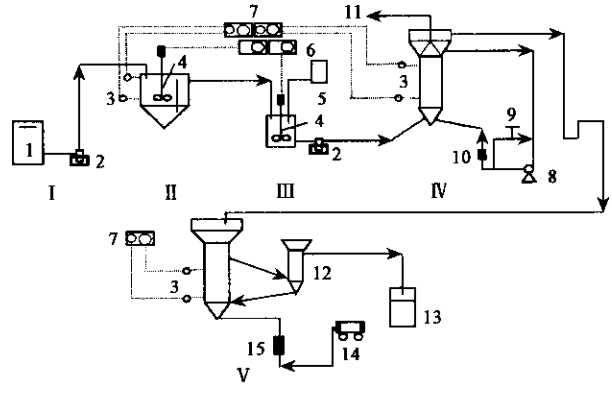

Fig.1 Schematic diagram of the experimental set-up

Ⅰ. influent part; Ⅱ. anoxic part; Ⅲ. neutralization part; Ⅳ. anaerobic part; Ⅴ. aerobic part; 1. wastewater tank, 2. peristaltic pump; 3. constant temperature heater; 4. stirrer; 5. dilute acid tank; 6. rotate speed controller; 7. temperature controller; 8. recycle pump; 9. circumfluence valve; 10. liquid flow meter; 11. biogas collector and separator; 12. sludge precipitator; 13. storage vessel; 14. air compressor; 15. gas flow meter

1.3 Analysis

Samples taken from reactors were filtered immediately. Analysis of TA was carried on a high performance liquid chromatograph(HPLC, Gilson, France). Aliquots of 25 μl were injected to the HPLC, running with mobile phase of acetonitrile/water (v/v) at 58/42, and an addition of 2 μl of concentrated H_3PO_4 per liter of solution. The separation was performed using an ODS-18 reversed phase column(Alltech, USA) at the flow-rate of 1.5 ml/min and column temperature of 25℃. An UV detector was used with the wavelength set at 254 nm. It is measured that TA retention time was at 4.57—4.63 min.

Table 2 Significant parameters for wastewater treatment

Reactor	T, ℃	A/W, m^3/m^3	SVI, ml/g	DO, mg/L	MLSS, g/L	Influent pH	Hybrid mode	Up-flow linear velocity, m/h
ATR	30	15—20	85	3.0—5.5	2.5—3.5	≤11.0	Gas-flow mixing	—
CSTR	30	—	60	0—0.3	3.6—4.2	≤11.0	Mechanical agitation	—
EGSB	33	—	22(bed)	—	15—17	6.8—7.5	Outside loop	3—5

Notes: A/W only for continuous flow operation

Analyses of other items were measured by the standard method (Editorial Board of Environment Protection Bureau of China, 1997). Simultaneously, COD was also tested with closed reflux spectrophotometric method(Guan, 2001).

2 Results and discussion

2.1 TA degradation by aerobic activated sludge

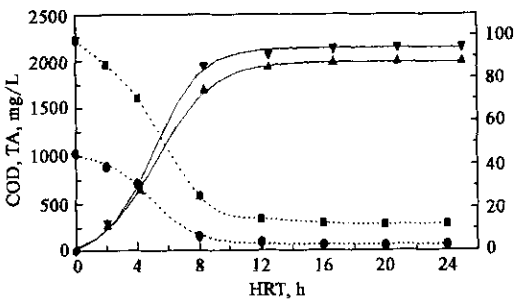

Fig.2 TA and COD removal in aerobic batch treatment of TPW-water

■ COD ● TA ▼η_{TA} ▲η_{COD}

The shapes of the COD and TA profile were very similar for all the experiments except that the removal efficiencies of TA(η_{TA}) were greater than those of COD(η_{COD}) in batches treatment under aerobic conditions. In Fig.2, TA and COD concentration and removal efficiencies are plotted as a function of HRT. The influent contained COD 2211 mg/L and TA 1022 mg/L. It was observed that η_{COD} was 84.7% at HRT 12 h and 87.2% at HRT 24 h, while the corresponding value for TA (η_{TA}) was 91.0% and 94.5% respectively. Briefly, more than 90% of TA was removed within a short time of 12 h. The corresponding HPLC patterns of TPW-water are shown in Fig.3.

Table 3 shows the typical results of continuous flow operation for a week. The influent COD ranged between 1664 mg/L and 2364 mg/L and the effluent COD varied from 240 mg/L to 324 mg/L with η_{COD} between 82.7% and 89.6%. Meanwhile, the influent TA between 500 mg/L and 800 mg/L led to the corresponding effluent TA less than 20.4 mg/L with η_{TA} between 96.5% and 98.7%. Obviously, η_{TA} was higher than η_{COD}. TA appeared to be readily degraded by aerobic activated sludge during continuous flow operation, as well as it did in the

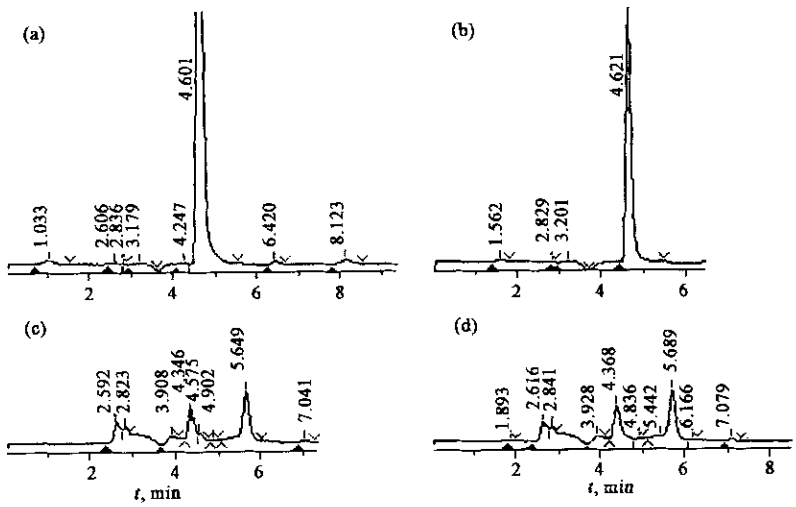

Fig.3 HPLC patterns of TPW-water in aerobic batch treatment

(a) HRT 0 h (sample diluted 10 times); (b) HRT 4 h (sample diluted 10 times); (c) HRT 8 h; (d) HRT 12 h

batch treatment. The COD equivalent of TA in the effluent was less than 30 mg/L, which only accounted for about 10% of the total COD of the effluent. Consequently, TA was not the chief pollutant being responsible for the effluent COD, and more attention should be paid on other organic pollutants when aerobic activated sludge process is used for TPW-water treatment.

2.2 TA degradation by anoxic or anaerobic activated sludge

TPW-water was treated in batches by activated sludge under anoxic conditions. As shown in Fig.4, less than 4.6 % of COD and 9.6% of TA were removed from wastewater after HRT 24 h.

Table 4 shows the results of TPW-water treatment under anoxic conditions with continuous flow. Even if HRT was increased from 10 h to 20 h, the turnover of COD kept below 9.2% while η_{TA} less than 6.5%. Further, η_{TA} did not increase along with the prolonged HRT.

Table 3 Typical results of aerobic treatment with continuous flow

Continuous operation, d		1	2	3	4	5	6	7
HRT, h				24			16	
COD, mg/L	Influent	2364	2129	2328	2307	2037	1664	1882
	Effluent	278	284	242	240	287	288	324
TA, mg/L	Influent	782		777		762	502	
	Effluent	20.4		16.2		19.0	17.5	
COD_{TA}/COD	Influent	50.0		46.4		52.0	41.9	
	Effluent	10.2		9.30		9.20	8.45	

Note: the COD equivalent of TA in wastewater is abbreviated as COD_{TA}

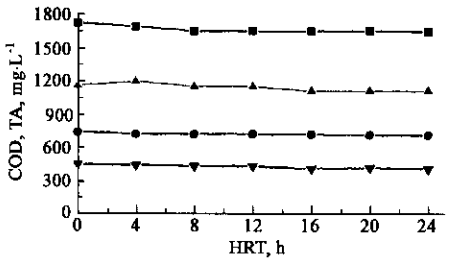

Fig.4 TA and COD removal in anoxic batch treatment of TPW-water

Batch 1: ■ COD, ● TA; Batch 2: ▲ COD, ▼ TA

Table 4 Typical results of anoxic treatment with continuous flow

HRT, h	COD, mg/L		TA, mg/L		η, %	
	Influent	Effluent	Influent	Effluent	COD	TA
10	1634	1583	843	823	3.1	2.4
16	2109	1914	1151	1076	9.2	6.5
20	1739	1705	945	906	2.0	4.1

The EGSB process was operated uninterruptedly in TPW-water treatment with a continuous flow for one year. As an example, Fig.5 gives the typical results for three weeks operation. The influent COD was from 1250 mg/L to 1943 mg/L and TA from 563 mg/L to 1141 mg/L. In the period of stable operation from 1st to 15th day, η_{COD} ranged between 27.1% and 68.0% while η_{TA} varied from 31.4% to 56.0%, correspondingly. It was also noted that η_{TA} and η_{COD} had a marked decrease with a lag of several days after the anaerobic system received a high influent COD shocking at 16th day. This illustrated that TA degradation and COD removal could be unstable in an anaerobic system when TPW-water quality changed greatly.

It is confirmed that activated sludge can hardly degrade TA in TPW-water under anoxic condition and TA remained as slowly biodegradable substrate under anaerobic conditions. Anoxic or anaerobic biological process cannot be effectively to removal TA from TPW-water.

2.3 TA degradation in combined biological process

The combined biological process was run continuously for two weeks, the typical results are given in Fig.6.

In the aerobic reactor, η_{TA} was over 93% and η_{COD} about 80%, the concentration of TA was below 16 mg/L so that it could not be well plotted in the figure. In the anoxic reactor, η_{COD} was about 10% and η_{TA} below 5%. In the anaerobic reactor, both η_{COD} and η_{TA} are between 40% and 50%.

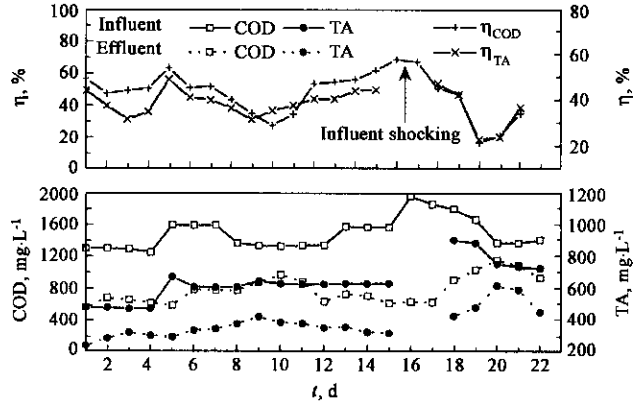

Fig.5 TA and COD removal in an EGSB reactor

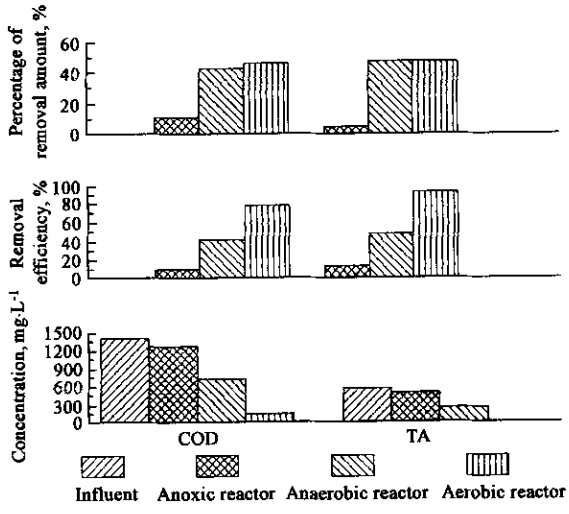

Fig.6 Performance of the combined biological process for TA and COD removal

The anoxic reactor only shared 11.5% COD, 5.1% TA of the total amount removed from the wastewater while the anaerobic reactor shared 43% COD, 47.2% TA and the aerobic reactor 45.9% COD and 47.7% TA.

η_{COD} and η_{TA} of the aerobic reactor were much higher than that of the anaerobic reactor, but two reactors shared approximate amount of removed COD or TA. It could not be neglected that the HRT of TPW-water in the anaerobic reactor was much longer than in the aerobic reactor.

The total removal efficiencies of COD and TA were 89.2% and 96.8% respectively. This illustrated that the combined biological process not only removed TA efficiently but also had a high performance for TPW-water treatment.

2.4 Influence of TA on BOD/COD of TPW-water

In order to measure the influence of TA on the degradability of TPW-water, the ratio BOD/COD (B/C) was conducted. Firstly, B/C of TPW-water was determined. Subsequently, pH value was adjusted below 2.0 so that most of TA could be separated from the wastewater after filter. Then, B/C was determined again. The results as well as the TA aqueous solution are shown in Table 5.

In general, higher B/C indicates better biodegradability of substrate or wastewater. TA aqueous solutions with COD 1015 mg/L and TA 649 mg/L had a high B/C of 0.64, that is, TA in aqueous solution qualified the readily biodegradable substrate. It can be seen that BOD of TPW-water was decreased 78% and B/C lowed markedly from 0.42 to 0.21 after TA separation from the wastewater. Clearly, TA is essential to increase B/C of the TPW-water.

Table 5 Influence of TA on BOD/*COD* of TPW-water

Sample	COD (average), mg/L	BOD (average), mg/L	pH adjusted	B/C (average)
TPW-water	1414	594		0.42
After TA separation	633	132	2.0	0.21
TA aqueous solution	1015	649		0.64

3 Conclusions

TA could be removed effectively and quickly from TPW-water by activated sludge under aerobic conditions while η_{TA} over 96.5% in a continuous flow reactor at HRT 16—24 h. But TA was difficult to be degraded by anoxic activated sludge with η_{TA} less than 6.5% at HRT 10—20 h. Under anaerobic conditions, TA could be degraded slowly over η_{TA} range from 30.7% to 56.0% in EGSB reactor. Among these biological processes, the aerobic one is the most effective to remove TA from TPW-water. TA was responsible for the majority of BOD in TPW-water. The higher concentration of TA conduced toward the better biodegradability of TPW-water.

Nomenclature:

ATR is the aeration tank reactor; A/W is the volume ratio of air to liquor, Nm^3/m^3; BOD is the biochemical oxygen demand, mg/L; HRT is the hydraulic retention time, h; B/C is the BOD_5/COD_{Cr}; MLSS is the mixed liquor suspended solid, g/L; COD is the chemical oxygen demand, mg/L; *SVI* is the sludge volume index, ml/g; COL is the color, unit; T is the temperature, ℃; CSTR is the continuous stirred tank reactor; TA is the terephthalic acid; DO is the dissolved oxygen, mg/L; η is the removal efficiency, %; EGSB is the expanded granular sludge bed.

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