Study on biodegradability of terephthalic acid in polyester fabric alkali-peeling process wastewater
Qiyong Yang, Zhongwei Wu and Chunyuan Tao

ABSTRACT
Terephthalic acid (TA) and ethylene glycol (EG) are the main pollutants in polyester fabric alkali-peeling process wastewater (PAP-wastewater). The biodegradability of TA is crucial to the deep treatment of PAP-wastewater. Batch and continuous experiments were adopted to study the biodegradation of TA in synthetic wastewater. In anoxic batch experiments TA began to degrade gradually after EG was depleted completely. However, in aerobic batch experiments the biodegradation curves of TA in the presence of EG were almost identical to those of TA in the absence of EG. The combined process of anoxic hydrolysis–acidification bioreactor (HABR) and aerobic hybrid membrane bioreactor (HMBR) was employed to treat synthetic PAP-wastewater in continuous experiments. When TA was fed as sole substrate, about 6.1% was removed in the anoxic HABR and 92.1% was biodegraded in the aerobic HMBR. When TA and EG were fed as substrate, only 1.9% of TA was biodegraded in the anoxic HABR and 96.6% of TA was removed in the aerobic HMBR. By contrast, most EG was removed in the anoxic HABR. The experimental results revealed that the combined process of anoxic HABR and aerobic HMBR was an attractive alternative for the treatment of PAP-wastewater and other similar wastewater.

Key words | biodegradability, hybrid membrane bioreactor (HMBR), polyester fabric alkali-peeling process wastewater (PAP-wastewater), terephthalic acid

INTRODUCTION
The alkali-peeling process is the pretreatment of polyester fabric before dyeing in order to improve the performance of polyester fabric. In the alkali-peeling process, unreacted sodium hydroxide (NaOH), terephthalic acid (TA) and ethylene glycol (EG) are produced by the saponification of polyethylene terephthalate with sodium hydroxide (Choe et al. 2005). The effluent from the process is called polyester fabric alkali-peeling process wastewater (PAP-wastewater). Various biological technologies are employed to treat wastewater containing TA, such as aerobic, anaerobic and combined biological processes.

Chidambara Raj et al. (1997) investigated the rates of aerobic biodegradation of acetic, benzoic, isophthalic, toluic acids and TA by a mixed bacterial culture. Amoco Corporation treated purified terephthalic acid wastewater with a three-stage aerobic activated sludge process before the 1980s (Lau 1978). However, the aerobic treatment of purified terephthalic acid (PTA) wastewater presented some disadvantages: long hydraulic retention time (3–5 days), high oxygen requirement and the possibility of sludge bulking.

In recent years, low-rate anaerobic pretreatment has been preferred to conventional aerobic activated sludge treatment of PTA-wastewater, and the investigations of anaerobic degradation of TA and anaerobic pretreatment of PTA-wastewater have increased markedly (Macarie et al. 1992; Cheng et al. 1997; Tsuno & Kawamura 2009; Zhu et al. 2010). Daramola et al. (2011) suggested that a one-stage thermophilic anaerobic reactor coupled with a coagulation–floculation pretreatment unit and an aerobic post-treatment unit could be techno-economically viable for PTA-wastewater treatment. Pophali et al. (2007) demonstrated that the combination of anaerobic–aerobic treatment was a techno-economic alternative to the two-stage aerobic process. Because the degradation process of TA would be inhibited by benzoic acid and acetic acid (Fajardo et al. 1997; Kleerebezem et al. 1999), a two-stage anaerobic reactor system was employed in the treatment of...
PTA-wastewater (Young et al. 2000; Grant et al. 2001; Kleerbezem et al. 2005).

However, the anaerobic degradation rates were low and lag phases prior to degradation of TA were long, ranging from 1 or 3 months in batch experiments to more than 1 year in full-scale reactors (Pereboom et al. 1993). Considering the disadvantages of aerobic and anaerobic treatments, as well as the characteristics of PAP-wastewater, an anoxic hydrolysis–acidification bioreactor (HABR) was employed to treat PAP-wastewater followed by an aerobic hybrid membrane bioreactor (HMBR) in this study.

MATERIALS AND METHODS

Seed sludge and reagent

The unacclimatised sludge for the experiments was collected from the return activated sludge (RAS) line (Municipal Wastewater Treatment Plant in Shanghai City, P. R. China), which had mixed liquor suspended solids (MLSS) of 3.5 g/L and a sludge volume index (SVI) of 150 ml/L. The HABR was initially seeded with an anaerobically unacclimatised sludge from the sewage treatment plant, which reduced the start-up time. TA, EG, (NH₄)₂SO₄, KH₂PO₄, Na₂HPO₄ · 12H₂O, MgSO₄ · 7H₂O, CaCl₂ · 2H₂O, FeSO₄ · 7H₂O, NaHCO₃ and CO(NH₂)₂ were AR grade, and were supplied by the Chinese medicine group Chemical Reagent Co., Ltd.

Batch experiments

In order to study the influence of EG on the aerobic biodegradation of TA, batch experiments with unacclimatised sludge were performed in 1,000 ml conical flasks covered with two layers of gauze. Substrates (in mg/L): TA(400), TA(400) + EG(60), TA(400) + EG(120), TA(400) + EG(240), TA(400) + EG(360) were added to each of five flasks. The activated sludge suspension was added to flasks according to F/M = 3.0 (F: TA concentration in mg chemical oxygen demand (COD); M: dry microbe in mg). During the experiment, COD and concentration of TA were measured every 12 hours. The basal medium used in batch experiments contained (in mg/L liquid volume): (NH₄)₂SO₄ (2500), KH₂PO₄ (1400), Na₂HPO₄ · 12H₂O (3600), MgSO₄ · 7H₂O (2500), CaCl₂ · 2H₂O (16.0), FeSO₄ · 7H₂O (2.0). All flasks were incubated at 30 ℃ under agitation on an orbital shaker at an equivalent stirring of 150 rpm.

All experiments were performed in duplicate in order to investigate the biodegradation of EG and its effect on the biodegradation of TA.

Continuous experiments

The pilot treatment process of continuous experiments consisted of two sequential reactors (HABR + HMBR), as shown in Figure 1. The HABR, which had a working volume of 12.5 L (125 × 250 × 400 mm), was equipped with fixed carriers and a electric agitator. The HMBR with a working volume of 10 L (220 × 140 × 325 mm) was filled with porous, flexible suspended particle carriers. A flat, hollow fiber membrane module with 0.4 m² of membrane surface area was immersed in the HMBR. The hollow fiber membranes were made of polyethylene with a pore size of 0.1–0.2 μm (Hangzhou Zheda Hyflux Hualu Membrane Technology Co. Ltd, China).

The synthetic wastewater was pumped to a head water tank with an overflow drain, which could keep a certain water level during the treatment process. Then the influent flowed into the HABR from the bottom. The wastewater remained in the HABR for 13.5 hours in anoxic conditions. The effluent of the HMBR was intermittently syphoned off by a peristaltic pump under a constant flux, and the transmembrane pressure was monitored by a pressure gauge. A suction mode of 10 minutes on and 3 minutes off was adopted. The suspended carriers flowed upward together.
with the fluid by aeration, which could remove the cake layer deposited on membrane surface. The characteristics of porous suspended carriers are shown in Table 1.

A steady-state condition was reached in 20–30 days by achieving a COD and TA removal rate of 78.1% and 70.5%, respectively. In the first phase of the reactor, from day 1–87, the system was fed with synthetic TA wastewater (TA as sole substrate), and in the second phase, from day 96–162, the system was fed with a synthetic mixture of TA and EG. The operational parameters are summarised in Table 2.

**Analysis methods**

The analysis of COD, biochemical oxygen demand (BOD₅) and mixed liquor suspended solids were according to standard methods (Editorial Board of Environment Protection Bureau of China 1997). Mixed liquor pH was measured with a pH meter. Dissolved oxygen was measured with YSI model 58, series 5700 (Yellow Spring Instrument Co. Inc.). TA was determined by high-pressure liquid chromatography (HPLC, LC-10Atvp, Japan) (Guan et al. 2003). EG was determined by gas chromatography (GC-2010, Japan) after aqueous samples had been pretreated.

**RESULT AND DISCUSSION**

**Effect of EG on the biodegradation of TA in aerobic conditions**

Batch experiments with unacclimatised activated sludge were carried out to study the effect of EG on the aerobic biodegradation of TA. The degradation curves of TA and its corresponding COD removal curves are presented in Figure 2. After a lag period of 38 hours, TA and COD began to decrease rapidly until TA was almost depleted after 62 hours. It should be noted that the biodegradation curves of TA in the presence of EG were almost identical with those of TA in the absence of EG, while there was a great difference in the removal curves of COD in the presence of EG and the absence of EG. There was a lag period of about 12 hours in the removal of COD in the presence of EG. The experiments were stopped when TA began to deplete at 36–38 h, at which point the residual EG in the culture solution was measured by gas chromatography. The results show that EG had completely been consumed, which indicated that EG was almost depleted before TA was converted into intermediate metabolites, that is, the microbes could feed on EG and TA at the same time.

Furthermore, in aerobic batch experiments the biodegradation curves of TA in the presence of EG were almost identical to those of TA in the absence of EG. So it was confirmed that EG did not inhibit the aerobic primary biodegradation of TA by its presence.

**Biodegradation of TA as sole substrate**

Figure 3 shows the treatment performance of TA in the biotreatment system. The total mean removal rate of TA was 98.2%. In the anoxic HABR there was a low biodegradability of TA with a mean removal rate of 6.1%. However, 92.1% of TA was removed in the aerobic HMBR. It indicates that the facultative aerobe has a very low activity in TA, which coincided well with the conclusions about the low biodegradability of TA in anoxic conditions. Guan et al. (2003) stated that the removal rate of TA in terylene artificial silk printing and dyeing wastewater was less than 6.5% in anaerobic conditions, but the removal rate of TA was over 96.5% under aerobic conditions. Zhao (1994) reported that TA was difficult to biodegrade under anoxic conditions in the treatment of terephthalic acid wastewater. But they did not investigate the low biodegradability of TA further.

**Table 1 | Characteristics of porous suspended carriers**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Density/ kg.m⁻³</th>
<th>Porosity/ %</th>
<th>Average pore size/mm</th>
<th>Configuration size/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>30</td>
<td>90</td>
<td>1.0–1.5</td>
<td>10 × 10 × 10</td>
</tr>
</tbody>
</table>

**Table 2 | Operational parameters of the continuous experiments**

<table>
<thead>
<tr>
<th>Operation time/d</th>
<th>Wastewater</th>
<th>TA/mg L⁻¹</th>
<th>EG/mg L⁻¹</th>
<th>Total COD/mg L⁻¹</th>
<th>SRT°/day</th>
<th>HRT°/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–87</td>
<td>TA wastewater</td>
<td>150–600</td>
<td>0</td>
<td>270–870</td>
<td>Infinite</td>
<td>13.5/10.8</td>
</tr>
<tr>
<td>96–162</td>
<td>(TA + EG) wastewater</td>
<td>550–700</td>
<td>150–500</td>
<td>1,020–1,690</td>
<td>50</td>
<td>13.5/10.8</td>
</tr>
</tbody>
</table>

°SRT: sludge retention time of MBR.
°HRT: hydraulic retention time; the former is HRT of HABR on average, the latter is HRT of HMBR on average.
It should be noted that the removal rate of TA showed no obvious change in the HABR when the concentration of TA in raw water increased from 200 to 600 mg/L. But in the HMBR the removal rate of TA showed a rapid increase. In order to investigate the anoxic biodegradation of TA in different HRTs, the feeding of the reactors was stopped on day 87, and then the HABR was operated as a recirculated batch for a period of 6 days, that is, the effluent from the HABR was pumped back to the HABR. The concentration of TA was measured every day. As shown in Figure 4, during that period about 52.7% TA and 34.4% COD were degraded. The results indicated that the facultative aerobe had a very low activity in TA.

It was confirmed that TA was barely biodegradable in anoxic conditions, but easily biodegradable in aerobic conditions.

**Biodegradation of TA in the presence of EG**

During the second phase of continuous experiments, the systems were fed with a synthetic mixture of TA and EG. The aim of the second phase of continuous experiments was to study the biodegradability of TA in the presence of EG. So in the experiments TA in the feed was kept at about 600 mg/L, and EG in the feed was increased gradually. The combined biological process was run continuously for 67 days, and the experimental results are illustrated in Figure 5.

The total mean removal rate of TA was 98.5%. The anoxic HABR only showed 1.9% TA removal, while the aerobic HMBR showed 96.6% TA removal. It illustrated that TA could be efficiently removed in the combined biological treatment process. By comparison, the total COD removal rate was about 85–88% in the two-stage cyclic lead-lag anaerobic hybrid system for the treatment of polyethylene terephthalate production wastewater (Grant et al. 2001). The removal efficiency of COD was only 57–64% in the expanded granular sludge bed process for terylene artificial silk printing and dyeing wastewater treatment (Guan 2005). Pophali et al. (2007) treated PTA effluent by an
anaerobic–aerobic process. The removal efficiency of COD was 62% at a volumetric loading rate (VLR) of 4–5 kgCOD/m³/d and an HRT of 1–1.2 days by upflow anaerobic fixed-film fixed-bed reactor.

In this study, the experimental results suggested that the combined process was efficient for PAP-wastewater treatment. The total removal rate of TA was beyond 95% on average, which was achieved at an HRT of 24.3 h.

Effect of EG on the biodegradation of TA in anoxic conditions

The aforementioned discussion indicated that the anoxic biodegradation rate of TA was very slow. In order to study if the addition of a cosubstrate to the influent could enhance the anoxic biodegradation of TA, EG was added to the reactors during the second phase of continuous experiment. The concentration of EG in the influent is shown in Table 2. Due to the fixed carrier and no sludge circulation, the biomass in the HABR remained between 2.1 and 3.2 g/L.

As mentioned above, the anoxic biodegradation rate of TA in the presence of EG was less than 1.9% on average. Figure 6 shows the effect of EG on the anoxic biodegradation of TA in continuous experiments.
biodegradation of TA. The removal rate of TA in the first phase (biodegradation of TA as sole substrate) was higher than that in the second phase (biodegradation of TA in the presence of EG).

In order to study the influence of EG on anoxic biodegradation of TA, the feeding of the reactors was stopped at the end of first and second phases (days 1–87 and 96–162 respectively), and then the HABR was operated as a recirculated batch for a period of 6 days, that is, the effluent from the HABR was pumped back to the HABR. The concentrations of TA, EG and COD were measured every day. The anoxic biodegradation of TA in the presence of EG is shown in Figure 7, which compares the biodegradability of TA in synthetic TA wastewater and synthetic (TA + EG) wastewater. There was a rapid decrease in COD as EG fell sharply, while TA hardly showed any degradation in (TA + EG) wastewater. When EG was depleted, TA began to degrade gradually. It should be noted that the biodegradation curves of TA and COD in TA wastewater were almost identical to those in (TA + EG) wastewater when EG was almost depleted.

From these experimental observations it was concluded that EG did not enhance the anoxic biodegradation of TA, on the contrary, it partially inhibited the biodegradability of TA in anoxic conditions. When the substrate was a mixture of TA and EG, only 1.9% of TA was biodegraded and most of EG was removed in the anoxic HABR. In anoxic batch experiments, TA began to degrade gradually after EG was depleted completely, and the biodegradation curves of TA as sole substrate were almost identical to those of TA in the presence of EG.

• TA was easily biodegradable in aerobic conditions. In the aerobic HMBR 92.1% of TA was removed in the absence of EG, while 96.6% of TA was removed in the presence of EG. EG did not inhibit the primary biodegradation of TA in aerobic conditions.

• The combined process of anoxic HABR and aerobic HMBR was efficient for PAP-wastewater treatment. The total removal rate of TA was over 95% on average at an HRT of 24.3 h.

REFERENCES


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