Treatment of Wastewater from Purified Terephthalic Acid (PTA) Production in a Two-stage Anaerobic Expanded Granular Sludge Bed System

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Abstract
The wastewater treatment with a two-phase expanded granular sludge bed (EGSB) system for anaerobic degradation of acetate, benzoate, terephthalate and p-toluolate from purified terephthalic acid (PTA) production was studied. The feasibility and effectiveness of the system was evaluated in terms of organic oxidation by chemical oxygen demand (COD), gas production, bacterial adaptability and stability in the granular sludge. Average removal efficiencies 93.5% and 72.7% were achieved in the EGSB reactors under volumetric loading rates of 1.0–15 kg-COD/m³/d and terephthalate and p-toluolate of 351–526 mg/L, respectively. Gas production reached total methane production rate of 0.30 L/g-COD under these conditions in the sequential EGSB reactor system. Higher strength influent COD concentration above 4.8 g-COD/L related to field conditions was fed to observe the disturbance of the EGSB reactors.

Keywords: Anaerobic treatment, EGSB, PTA, Two-phase, Wastewater

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1. Introduction

PTA (1,4-benzenedicarboxylic acid, C₆H₄(COOH)₂) is purified via hydrogenation of crude terephthalic acid and widely used as the main raw colorless solid material in the manufacturing of various petrochemical products [1,2]. A high strength organic PTA wastewater is generated from the oxidation and purification processes during the PTA manufacturing procedures. The catalyst recovery section, cleaning and washing water, PTA scrubbing water, and distillate acid water are the major sources of wastewater generation. The PTA scrubbing section generates the maximum quantity of wastewater corresponding to 5–20 kg-COD/m³ with 3–10 m³ wastewater/t PTA production and contains terephthalate, acetate, benzoate and p-toluate [3,4]. Accordingly, terephthalate, acetate, benzoate, and p-toluate are the major organic contaminants required to be removed from the PTA production wastewater and trimellitic acid, o-phthalic acid and 4-carboxybenzaldehyde are also found in the wastewater [5,6].

Anaerobic wastewater treatment was gradually developed to be applied for treatment of more complicated and higher strength organic wastewater such as aromatic compounds in the more complex industrial PTA wastewaters [7, 8]. Considering the constituents of PTA production wastewater, acetate and benzoate are anaerobically readily degradable compounds but terephthalate and p-toluate are hardly degradable contaminants that can only be degraded at very low rates. Further, the concentration of benzoate and acetate in the PTA wastewater hinder the biological degradation of terephthalate and p-toluate during the treatment [9]. When acetate and benzoate were excluded in the influent from anaerobic bioreactors effective terephthalate degradation was achieved. Due to its poor degradability, P-toluate was also biodegraded only at very low rates in anaerobic reactions [10]. Kleerebezem et al.[11, 12] reported that the slow biodegradation of terephthalate was the main reason for the complex inhibition effects of acetate and benzoate on the inefficient degradation of terephthalate when
treating artificial PTA-wastewater. Kleerebezem et al. [13] also reported that degradation of
terephthalate was rate limiting during anaerobic treatment of PTA-wastewater containing
acetate, benzoate, and terephthalate in lab-scale UASB-reactors.

On the other hand, due to low 5–20% of the volumetric loading rate by \( p \)-toluate, high
volumetric loading rate and removal efficiency were not affected by \( p \)-toluate during
anaerobic pre-treatment. Thus major problems in the anaerobic treatment of PTA production
wastewater were chemical inhibition effects and shock loads [14, 15]. However, benzoate,
terephthalate, and \( p \)-toluate concentrations in PTA production wastewater were not toxic to
acetoclastic and hydrogenotrophic methanogens at the levels encountered in PTA production
wastewater [16].

Kleerebezem and Lettinga [1] suggested a two-stage anaerobic system in order to prohibit
inhibition of terephthalate degradation by acetate and/or benzoate under the operational
circumstances by spatial separation of acetate and benzoate degradation in the earlier stage
and degradation of terephthalate (and \( p \)-toluate) in the post stage. Hybrid and contact
processes for PTA wastewater treatment showed COD reductions of 79–92 and 71–84% [17].
Up-flow anaerobic sludge blanket (UASB) and expanded granular sludge bed (EGSB)
systems are two well known high-rate anaerobic wastewater treatment systems, where cluster
of microorganisms are aggregated in dense granular sludge bed. EGSB system is a
modification of the traditional UASB system to obtain the better hydrodynamic function, so
EGSB improved the Feeding and the contact between the wastewater and the sludge bed in
the system [18, 19]. To overcome chemical inhibition and shock loads for the treatment of
PTA-production wastewater, expanded-bed granular activated carbon anaerobic reactor was
applied [20]. However the high-rate anaerobic bioreactor system has not yet fully developed
for the complex process dynamics and some important metabolisms of the involved
microorganisms and thus operation of a full-scale system is still in a challenging stage [9].
In this study, anaerobic treatment of a real PTA production wastewater with a two-stage EGSB system was tested for chemical inhibition of acetate, benzoate, \( p \)-toluate, and terephthalate. Shock loadings including the use of various Feedture ratios of low and high level concentrations of PTA production wastewater were tested. The results obtained with the high-rate two-stage EGSB reactor system is discussed whether the most practical applicability for high-rate anaerobic spatial treatment of PTA production wastewater.

2. Materials and methods

2.1. EGSB Reactors System

A process diagram of the two-stage anaerobic EGSB system is shown in Fig. 1. Two 6 L identical EGSB reactors (I-EGSB and II-EGSB) with a diameter of 80 mm and height of 1.2 m were made of polyacrylate resin.

Fig. 1. Process diagram of the two-stage EGSB reactors system.
To expand the granular sludge biomass, the wastewater in the EGSB reactor was circulated from the top to the bottom and the working volume of 5.0 L resulted in both EGSB reactors. The water temperature in both I-EGSB and II-EGSB reactor was maintained at 34–36±1 °C using electric heating coils. The biogas from both reactors was collected from the top of the reactors by the gas-holders. The influent and recirculation flow were Feded in a Feeding organic acid tank (T-I) prior to introduction into I-EGSB. The influent pH was buffered to be 6.7 with NaHCO₃ and fortified with nutrients (NH₄Cl and KH₂PO₄, 5:1). Nutrient COD ratios were maintained at 200:5:1 (COD: N: P). The I-EGSB effluent was collected in an external Feeding organic acid tank (T-II) prior to introduction into the second stage (II-EGSB). The first stage reactor (I-EGSB) was used for the stabilization of a volatile fatty acid (VFA)-based PTA production wastewater consisting of acetate and benzoate to a total of 4.9 g-COD/L. The second stage reactor (II-EGSB) of the two-stage anaerobic system was adjusted to maintain the terephthalate degrading granular sludge. The system was operated at various VLRs to obtain the optimized performance of the EGSB system.

2.2. Start-up and Operation of the EGSB System

The I-EGSB and II-EGSB were each inoculated with granular sludge from an anaerobic digester of sewage treatment plant to provide granular sludge as a carrier material for the terephthalate and p-toluate degrading suspended culture capable of degrading the constituents in the PTA production wastewater.

Both reactors were inoculated with 20 g VSS/L biomass (volatile suspended solids) and further stabilized with 30 g VSS/L biomass at the full development of the granular sludge bed. The sludge was continuously fed for 10 d using 10 g/d of sucrose, 250 mg/d of nitrogen as
NH₄Cl, and 50 mg/d of phosphorus as K₂HPO₄. The sludge for EGSB-II was acclimatized by gradual introduction of the PTA wastewater discharged from a PTA manufacturing plant (KP Chemical, Ulsan, Korea).

In the first phase, to induce granular sludge bed development on the reactors with the recirculation pump of which flow rate was maintained at 1.5–15 L/h, the I-EGSB and II-EGSB were operated in a batch mode. After one month from the initial phase start-up, the operation was switched to a continuous mode (operation 1). In the first phase, feeding flow rate was 0.35 L/d which is corresponding to the hydraulic retention time (HRT) of 14.3 d. Then, the feeding flow rate was gradually increased up to 20 L/d (HRT = 6.0 h) for 300 days operation. The superficial velocity of I-EGSB and II-EGSB applied through the recirculation with T-I and T-II was increased from 0.52 to 2.9 m/h. In time the VLR of the reactor was gradually increased up to 15 kg-COD/m³/d for 10 months with increasing the influent flow rate. The first operational conditions in the two-stage EGSB system are listed in Table 1.

**Table 1. Physico-chemical characteristics of operation 1 in the two-staged EGSB system**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Influent</th>
<th>EGSB-I</th>
<th>EGSB-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating time (d)</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Flow rate (L d⁻¹)</td>
<td>0.30–16</td>
<td>0.30–16</td>
<td>0.30–16</td>
</tr>
<tr>
<td>Superficial velocity (m h⁻¹)</td>
<td>0.52–2.9</td>
<td>0.52–2.9</td>
<td>0.52–2.9</td>
</tr>
<tr>
<td>Terephthalate (mg L⁻¹)</td>
<td>48–503</td>
<td>46–253</td>
<td>25–68</td>
</tr>
<tr>
<td>p-toluate (mg L⁻¹)</td>
<td>40–466</td>
<td>35–430</td>
<td>23–64</td>
</tr>
<tr>
<td>Acetate (mg L⁻¹)</td>
<td>106–1708</td>
<td>90–115</td>
<td>10–41</td>
</tr>
<tr>
<td>Benzoate (mg L⁻¹)</td>
<td>105–730</td>
<td>45–92</td>
<td>9–18</td>
</tr>
<tr>
<td>COD (mg L⁻¹)</td>
<td>468–4855</td>
<td>293–1502</td>
<td>107–216</td>
</tr>
<tr>
<td>VLR (kg COD m⁻³ d⁻¹)</td>
<td>1.9–15</td>
<td>1.3–6.8</td>
<td>0.4–1.2</td>
</tr>
</tbody>
</table>

The system was fed to evaluate the shock load impacts on the system from fluctuations of the influent concentration with 3 different PTA production wastewater containing a Feedture of high and low level concentrations in the ratios of 1:74 (Feed 1), 2:73 (Feed 2) and 3:72 (Feed 3) comparable to those possibly found in PTA production wastewater (the 2nd
operation). The second operational conditions in the two-stage EGSB system are listed in Table 2. Initial feeding flow rate of 18 L/d corresponding to the HRT of 6.7 h was gradually increased up to 20 L/d (HRT = 6.0 h) for 40 d operation of each Feed. The anaerobic EGSB reactors were further operated over 4 months for the fluctuation test of the EGSB under shock load conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Feed1 (1:74)</th>
<th>Feed2 (2:73)</th>
<th>Feed3 (3:72)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating time (d)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Flow rate (L/d)</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Terephthalate (mg/L)</td>
<td>448–503</td>
<td>536–578</td>
<td>624–678</td>
</tr>
<tr>
<td>p-toluate (mg/L)</td>
<td>424–435</td>
<td>455–467</td>
<td>533–541</td>
</tr>
<tr>
<td>Acetate (mg/L)</td>
<td>823–852</td>
<td>727–748</td>
<td>642–653</td>
</tr>
<tr>
<td>Benzoate (mg/L)</td>
<td>679–659</td>
<td>579–591</td>
<td>481–497</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>3904–3926</td>
<td>3927–3951</td>
<td>3953–3972</td>
</tr>
<tr>
<td>VLR (kg-COD/m³/d)</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

2.3. Analytical Methods

A HPLC (Ultimate 3000, DIONEX) equipped with UV/Vis-detector (VWD3400, DIONEX) was used to analyze all organic contaminants (except acetate) in the PTA wastewater. The Agilent C18 (250 mm x 4.5 mm) separation column with packing size of 5 μm and the detection wavelength of 230 nm was used. A carrier liquid at the flow rate of 1 mL/min with a Feedture of methanol-acetic acid (4:6 v/v) was used. A Hewlett Packard gas chromatograph (model HP 6890) equipped with a flame ionization detector and a capillary column (HP-INNOWAX, 30m x 0.32mm i.d.) was used to determine acetic acid. The temperature profile was controlled initially 60°C for 5 min, and then adjusted to 300 °C at the rate of 5 °C/min. A carrier gas consisting of nitrogen saturated with formic acid was used at the flow rate of 2 ml/min. For the analysis of TSS and VSS in sludge samples, and COD measurements followed the directions in Standard Methods [21]. The biogas production was monitored each
day by collecting the volume and composition data of the biogas collected in the gasholder. A HACH model DR4000 was used to measure alkalinity. The liquid sample pH was measured by using an ORION model 3STAR (Orion, USA) pH meter.

3. Results

3.1. Efficiency of a Sequential Two-stage EGSB System

The removal of acetate and benzoate in the first stage can enhance terephthalate and p-toluate degradation in the second stage because strongly fluctuating acetate and benzoate loading rates primarily can affect the biodegradation of terephthalate and p-toluate. Acetate and benzoate in the PTA production wastewater are easily biodegradable organic constituents but biodegradability of terephthalate and p-toluate is unclear. As a consequence, anaerobic degradation of terephthalate and p-toluate in the second stage is preferred [13, 17]. Curves of influent VLR and COD concentration in the two-stage anaerobic EGSB system is designated in Fig. 2.
Fig. 2. Curves of influent VLR and COD concentration in the two-stage anaerobic EGSB system.

Until 50 days of feeding from start up in the first phase of operation as shown in Fig. 2, influent COD of some acetate and benzoate was incompletely degraded in I-EGSB and was introduced into II-EGSB during this period. This resulted in the relatively high effluent COD concentration of terephtalate and p-toluate in II-EGSB (Fig. 2(b)). After 50 days, the VLR was gradually increased step by step up to 15.0 kg-COD/m$^3$/d and this condition was maintained for up to 250 days. In the first phase of operation, the feeding period from 50 to 140 days, it seemed that most organic constituents except terephtalate and p-toluate were almost degraded in I-EGSB although some unexpected disturbances were observed due to VLR increase.
The total COD concentration of PTA production wastewater was average 7.2 g-COD/L, and VLR with acetate and benzoate corresponding to 75%–85% of the total was reduced in the first stage of the two-stage reactor system at very high rates (< 15 kg-COD/m³/d), while VLR with terephthalate and p-toluic acid was reduced in the 2nd stage at moderate rates (average 1.5 kg-COD/m³/d) as shown in Fig. 2(a) and 2(b), respectively.

The optimized COD reduction efficiency of 93.5% resulted at 6 h of HRT with high concentrations of granular sludge biomass (up to 30 g VSS/L) when the two-stage EGSB system was operated under maximum VLR of 15 kg-COD/m³/d. Thus the optimized COD reduction efficiencies were obtained to be considerably higher than those in a previous study with UASB reactors [12].

3.2. Biogas Production

The emissions of biogas were observed during 270 days of operation under a direct relationship with the volatile solids content. Biogas production was not obtained within 10 days during start-up from the I-EGSB reactor, although some COD was reduced. Thus the acclimation time to degrade organic constituents in the influent seems to be required in the first stage biogas production under newly imposed conditions. After gas production started at day 11, more steady daily gas volumes started to be obtained. If a steady-state condition is satisfied the methane production rate should be strongly correlated with the COD removal rate. The methane production from the two-stage EGSB during the continuous operation is shown in Fig. 3.
After 30 days of continuous operation of the two-stage EGSB process, methane biogas started to be produced gradually and increased rapidly. The steady-state methane production rates were obtained about 0.27 and 0.04 L/g-COD from I-EGSB and II-EGSB, respectively. The total methane production rate at the steady-state condition from the EGSB reactors reached to the maximum of 0.30 L/g-COD after about 135 days operation although some observed fluctuations. The methane yield obtained with the EGSB reactor is close to the stoichiometric value (0.35 L/g-COD); this means that the most COD reduced was actually converted to methane, and much less accumulation of influent organic constituents occurred.

After 120 days operation of the EGSB process, the methane biogas yields from I-EGSB and II-EGSB were stabilized to be enough for the true steady-state conditions finally achieved for the optimized operating conditions. The stabilized methane biogas yields in I-EGSB and II-EGSB were calculated to be about 0.27 and 0.04 L/g-COD, respectively, both of which were rather lower than the theoretical methane yield value of 0.35 L/g-COD. The maximum methane biogas production rates achieved in each stage of EGSB process were
0.30 and 0.04 Lg-COD, respectively.

3.3. Microbial Feature in the Sludge Granules

A SEM model HITACH S-4800 with an ion sputter model E-1045 (15A, 60 sec) was used to image the morphological characteristics of granules for analysis of the microbial distribution within granular sludge in EGSB reactors. Fig. 4(a) and 4(b) showed the different surface and inside images of the granules of I-EGSB and II-EGSB.

![SEM images of granules](image)

Fig. 4. Scanning electron micrographs of granule in EGSB reactors: (a) I-EGSB surface and inside, (b) II-EGSB surface and inside.

From the SEM images of the granules, where it can be recognized that more densed biofilm with smooth surface was noticed at the I-EGSB granule while a rather coarse surface
at the II-EGSB granule compared to the I-EGSB granule was imaged. Baloch et al.[22] reported that methanogens are usually acclimated in the favorable conditions observed for the I-EGSB granule and acidogens are favorable of the II-EGSB granules.

However, the superficial organic compounds biodegradation characteristics of the I-EGSB and II-EGSB granules were quite similar to each other. Therefore their organic compounds biodegradation rates could be clearly discriminated in that biodegradation rate for acetate and benzoate with the I-EGSB granule was faster than that of the II-EGSB granule whereas vice versa for biodegradation rate of terephthalate and p-toluate. Thus the granular biomass concentrations in both reactors during start-up period were almost same; it could be noticed that degradation rates might be different due to the spatial distributions of microorganisms within the granules, which could be varied depending on the concentrations of the influent organic compounds applied to the individual reactors.

3.4. Fluctuation Test with Higher Constituents in Influent

The responses of the system to shock loads of influent are designated in Fig. 5 with the COD reduction efficiency and effluent concentrations of terephthalate and p-toluate in the PTA wastewater during the fluctuation test. Fluctuation test with highly concentrated raw waste was conducted for the responses of the system to shock loads with PTA wastewater containing a mixture of higher constituents in the ratios of 1: 74 (Feed 1), 2: 73 (Feed 2) and 3:72 (Feed 3), which is comparable to the concentrations possibly found in PTA production wastewater as shown in Table 2.
Fig. 5. The responses to the influent disturbance of the two-stage EGSB system during fluctuation test (a) for Feed 1 (b) for Feed 2 (c) for Feed 3.
During 300 day of operation the influent of a mixture of high and low level concentrations was supplied with the ratio of 2:73 for Feed 2 and 3:72 for Feed 3 to test whether the increased concentration of organic constituents in influent would disturbance the efficiency of PTA production wastewater treatment. During these tests the maximum volumetric loading rate was increased to 7.5 kg-COD/m³/d, the VLR reduction efficiency reached a stable value of approximately 12.9 kg-COD/m³/d. During 100 days for Feed 1 the influent of a mixture with high and low level concentrations in the ratio of 1:74 was supplied to the system. The COD removal capacity and effluent concentrations of terephthalate and p-toluate under the condition of Feed 1 are shown in Fig. 5(a). Condition of Feed 1 contributes to the system resulting in increasing 11–15% of influent terephthalate and p-toluate concentrations in I-EGSB. Even with the fluctuation in the influent concentration, COD accumulated in the effluent to a maximum range of only 108–293 mg-COD/L, and the COD reduction efficiency was maintained as high as 93.2% and average 90.5%. Terephthalate concentration of 448–503 mg/L in I-EGSB had decreased to less than 6 mg/L in the effluent of II-EGSB. Terephthalate and p-toluate inhibited no microbial groups associated with the earlier stage of benzoate and acetate degradation in I-EGSB. The influent shock loads did not affect the degradation of either acetate or benzoate but COD removal efficiency was decreased in the system.

For Feed 2 test a mixture of high and low level concentrations in the ratio of 2:73 was fed to I-EGSB. Due to the increased COD loading rate, the COD reduction was affected to be poor. The COD reduction efficiencies of average 89.6% were obtained under the VLR of 15 kg-COD/m³/d during Feed 2 test. The observed results of Feed 2 test are shown in Fig. 5(b). Before terephthalate concentrations in the influent were increased to 436–578 mg/L, degradation of benzoate and acetate were maintained stably and initially terephthalate degradation in I-EGSB was not obtained. However terephthalate concentration of less than 11 mg/L in the effluent was maintained in II-EGSB throughout Feed 2 test. The influent...
fluctuation with shock-loads resulted in minor decrease in the COD removal capacity to 12.7 kg-COD/m³/d.

During Feed 3 test the terephthalate concentration in the effluent of I-EGSB was sustained to be similar as that in the influent at the start up. Thus the treatment efficiency was worsened after a further increase in the COD and terephthalate concentrations of 3963 and 678 mg/L in the influent for Feed 3 test, respectively. The effect of fluctuations by the increased mixture ratio of the influent for Feed 3 test was shown in Fig. 5(c). The average COD removal efficiency of 86.8% observed from Feed 3 test was lower than that of Feed 2 test and even much lower to that of Feed 1 test. As can be seen in Fig. 5(c), terephthalate concentration in the effluent was not declined as much as the previous tests after the deterioration of Feed 3 test. During Feed 3 test the influent was fed steadily to the system with COD loading rate of 15 kg-COD/m³/d, while removal efficiency was declined further to COD reduction capacity of 11.9 kg-COD/m³/d. The lowest COD removal efficiencies for Feed 3 test may be caused by the fact that the influent concentration of terephthalate and p-toluate was average about 19.5% higher than that of Feed 1 test. The COD removal efficiencies obtained during 3 Feed tests revealed that the overall reduction efficiencies worsened to some extent after introducing the highly concentrated PTA production wastewater. This result seems to be related to the extent of effluent concentration of terephthalate from I-EGSB of which trend is different from those around the Feed 1 and Feed 2 fluctuations.

4. Discussion

There is a better hydraulic distribution of the effluent in EGSB system because the granular sludge in the EGSB reactor is distributed in its entire volume, while in a UASB reactor the sludge is located at the bottom, forming a sludge blanket. Thus the EGSB reactor was much better than the UASB reactor in treating PTA production wastewater at the optimized rates of
VLR (average 7.2 kg-COD/m³/d) with superficial velocity of 3 m/h and a better Feeding of the granular sludge owing to an increase in the biogas production, which would improve substrate transfer.

If higher granular biomass concentration is obtainable, high rate degradation of acetate and benzoate in anaerobic system can be achieved within 1 month, but start-up of a UASB reactor using suspended methanogenic biomass may take much longer [11]. Due to the higher gas production rates per unit of reactor surface, a full scale UASB reactor may not be feasible to retain the high biomass concentrations (> 45 g VSS/L). However, EGSB reactors show steady granular sludge particulate expansion by high superficial velocities (2–15 m/h), resulting in the better gas liquid separation capacity [3]. Fajrado et al.[16] reported that terephthalic acid and aromatic compounds (dimethylterphthalate) resulted no inhibition effects to anaerobic treatment of easily biodegradable compounds (acetic, benzoic and formic acids) remaining in PTA wastewater during 40–50% COD removal by anaerobic digestion system.

The microbial population of involved granule culture was so fluctuate to the changes of the operating conditions, therefore more sufficient time should have been provided in order to achieve a true steady-state for soluble pollutant dynamics. The hydraulic characteristics of the EGSB reactor favored degradation of acetate and benzoate in the influent and conversion of soluble organic constituents to methane, reducing wastewater potential toxicity. Due to the affection of actual concentrations of acetate and benzoate in I-EGSB to the terephthalate and p-toluate removal capacity, the elevated acetate and benzoate loading rates in the first phase must have inhibited degradation of terephthalate and p-toluate in I-EGSB.

In the two-phase system, the removal of the organic constituents in the first phase would first result in the depletion of the readily biodegradable compounds like acetate and benzoate, as long as the acetate and benzoate levels are controlled in the first phase less than the treatment capacity of the second phase. This condition would provide a more favorable
environment for the terephthalate and p-toluate degrading microorganisms in the second phase. Once these microorganisms are more activated in the second phase due to the favored environment, the syntrophic bacteria would maintain an enhanced treatment capacity even though the organic loading rate is increased.

The acetate and benzoate degradation rate in I-EGSB was increased highly enough to sustain the terephthalate and p-toluate degradation rate over 80% in II-EGSB. Under the two-phase EGSB system, the acclimation process in II-EGSB enhanced the seeded biomass originally containing some microorganisms and their degrading capability of terephthalate and p-toluate. Accordingly, it seems that the two-single phase process would be favorable for the PTA wastewater treatment in the case that even operating VLR is increased.

Joung et al. [10] showed that the anaerobic degradation of terephthalate and p-toluate seems to be adversely affected by the presence of acetate and benzoate. The main advantage of the two-phase anaerobic reactor system was reduction of the lag-phase prior to terephthalate and p-toluate degradation in the second phase. Benzoate is also known to inhibit the terephthalate degradation [16]. Furthermore, high conversion rate was also achieved by the high concentrations of granular sludge biomass (up to 30 g VSS/L) sustained in EGSB reactors. Thus the volumetric COD reduction abilities are considerably higher and this study evidently shows that high-rate treatment of a mixture of acetate, benzoate, p-toluate and terephthalate is feasible with the two-phase EGSB system.

The EGSB system may therefore be the most suitable for practical implementation of high-rate anaerobic treatment of PTA production wastewater. The results showed in this study evidently suggest that high rate pre-reduction of acetate and benzoate in the two-phase anaerobic EGSB system is a feasible application for PTA-wastewater. As a consequence, the two-phase anaerobic EGSB system for this study was affordable to adopt with sequential two EGSB-bioreactors in series.
5. Conclusions

The following conclusions can be inferred based on this study:

· Due to high concentrations of granular sludge biomass (up to 30 g VS/L), much higher volumetric reduction rate (93.5% of 15 kg-COD/m³/d) was obtained, resulting high rate degradation of acetate and benzoate in the first phase with a comparatively smaller reactor volumes. Therefore EGSB reactor system may be feasible for successful practical implementation of high-rate anaerobic pre-treatment of PTA production wastewater.

· Due to pre-removal of acetate and benzoate in the first stage, terephthalate degrading capacity in the second stage can be enhanced at prolonged SRT-values. Thus main advantage of the two-phase anaerobic EGSB system is spatial separation for reduction of acetate and benzoate prior to terephthalate and p-toluate degradation in the second phase.

· The fluctuating acetate and benzoate loading rates primarily affect the terephthalate and p-toluate removal capacity and concentrations of acetate and benzoate of the effluent in the second phase can also be minimized. Accordingly, anaerobic degradation of terephthalate and p-toluate in the second phase remains to be preferred.

· Influent flow with sustaining up-flow superficial velocity of 2 m h⁻¹ resulted continuous expansion of granular sludge bed, and enhanced gas–liquid separation in EGSB reactors with methane gas production of 0.30 L/g-COD.

· Influent concentration of organic compounds may have a large impact on the microbial ability needed for COD reduction of the anaerobic treatment system if an average overall concentration of 3939 mg-COD/L (Feed 2) can be applied in a phased EGSB reactor as an
optimum concentration during fluctuation test.,

- The high influent concentrations tested in Feed 3 can be more difficult to be reduced in a full-scale EGSB reactor. Because the applicability of the higher concentration depends on the granular sludge biomass concentrations that can be maintained in the reactor due to requiring the higher biomass rates per unit of reactor-surface.

- The time needed for start-up of the anaerobic treatment reactor may be affected by the availability of granular sludge biomass for biodegradation of organic constituents in the reactor.

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References


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Fig. 1. Process diagram of the two-stage EGSB reactors system.

Fig. 2. Curves of influent VLR and COD concentration in the two-stage anaerobic EGSB system.

Fig. 3. The profile of methane production from EGSB.

Fig. 4. Scanning electron micrographs of granule in EGSB reactors: (a) I-EGSB surface and inside, (b) II-EGSB surface and inside.

Fig. 5. The responses to the influent disturbance of the two-stage EGSB system during fluctuation test (a) for Feed 1 (b) for Feed 2 (c) for Feed 3.