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Performance evaluation of anaerobic fluidized bed reactors using brick beads and porous ceramics as support materials for treating terephthalic acid wastewater

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ABSTRACT

This study evaluated two different porous support materials (brick beads and porous ceramics) used in rapid mass-transfer anaerobic fluidized bed reactors (AFBRs) for treating terephthalic acid wastewater. The AFBRs, denoted as *R*1 (containing brick beads) and *R*2 (containing porous ceramics), were inoculated with anaerobic sludge. Results showed that the system organic loading rate increased from 7.37 kg COD/(m^3 d) to 18.52 kg COD/(m^3 d) over a period of 73 d. During the steady period, *R*2 showed better performance than *R*1. The chemical oxygen demand removal efficiency and total alkalinity removal efficiency of *R*1 were 65–75% and 60–70%, whereas those of *R*2 were 75–88% and 72–84%, respectively.

Keywords: Fluidized bed reactor; TA wastewater; Porous support; Anaerobic treatment

1. Introduction

Pure terephthalic acid (PTA) is one of the most important manufactured petrochemical products in the world. It is used in manufacturing polyester fibers, molded resins, and polyethylene terephthalate (PET) bottles. Thus, wastewater with a high level of COD is generated during PTA production. In general, the wastewater generation varies from 3 to 10 m^3 per ton of PTA produced and is equivalent to 5–20 kg COD/m^3 [1].

Biological processes for wastewater treatment, especially anaerobic processes, are widely accepted as commercial methods for treating high-strength organic wastewater. Anaerobic treatment presents a number of advantages, such as low nutrient requirements, low surplus sludge production, and ability to achieve a high degree of purification with high organic load feeds [2–5]. PTA wastewater was usually treated using aerobic activated sludge process [6–8]. Since the 1990s, anaerobic treatment methods have been gradually introduced in PTA wastewater treatment plants because of advantages, such as low energy requirement and lower surplus sludge production [9,10]. However, one of the biggest problems in anaerobic treatment is the loss of biomass in systems with a high hydraulic loading rate.

In recent years, anaerobic fluidized bed reactors (AFBRs) have attracted considerable interest as an alternative to the conventional suspended growth and

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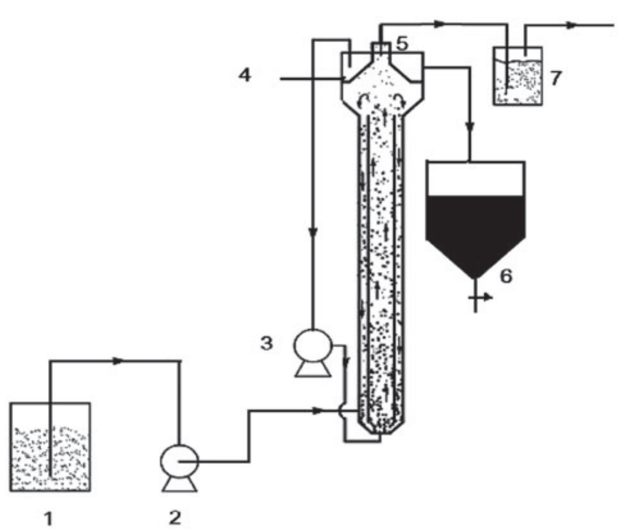
fixed-film wastewater treatment processes because of their high performance efficiency. AFBRs have been demonstrated in various studies to be feasible for treating different wastewaters [11–15]. In an AFBR, the support material can enable the reactor to retain high biomass concentrations and thus, operate at a significantly shorter hydraulic retention time (HRT). Fluidization also overcomes operating problems, such as bed clogging and high pressure drop, which occur when such porous supports are used in a packed bed reactor [16–18]. This study focused on the degradation of high-strength purified terephthalic acid (PTA) wastewater in rapid mass-transfer AFBRs. Two different porous support materials were tested. Their physical properties and treatment performance were compared.

2. Materials and methods

2.1. Anaerobic fluidized bed reactor

Fig. 1 shows a schematic diagram of the laboratory-scale FFBR used for the PTA wastewater treatment in the current study. The reactor was made of acrylic glass and consisted of an outer cylinder, with 7.0 cm ID, 77.0 cm length, and an inner cylinder, with 3.4 cm ID, 71.0 cm length. The upper end of the reactor was equipped with a gas-liquid-solid separator and an inclined plate separator to reduce the liquid velocity and prevent particle loss. A cone was installed at the lower part of the outer cylinder at a 55° inclined angle to attain smooth particle circulation.



(1. Influent tank, 2. Diaphragm metering pump, 3. Reflow pump, 4. Gas-liquid-solid separator, 5. Gas export, 6. Secondary settling tank, 7. Liquid seal tank)

Fig. 1. Schematic diagram of the fluidized bed reactor.

The effluent was recycled through a recycling pump connecting the effluent outlet and the feed inlet during operation. The reactor was filled with the solid support material up to 35% of its active volume. The temperature in the AFBR was maintained at 25℃. In the up-flow area, the high-density supports and wastewater were both flowed upward at a high fluidized velocity, thereby increasing the relative inter-phase turbulence intensity of the up-flow area. In the down-flow area, the supports and wastewater rapidly subside under gravity because of the high-density supports, thereby increasing the relative inter-phase turbulence intensity of the down-flow area. Consequently, the mass-transfer velocity and efficiency of the whole reactor was increased.

2.2. Support materials

Brick beads mainly composed of SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO were used as the supports for biomass immobilization in an AFBR. The brick beads were chemically pretreated to enlarge the diameter of pores. The chemical pretreatment consisted of soaking the beads in sodium hydroxide for 10 min, rinsing with water for 5 min, and oven drying at 80℃.

The porous ceramics were processed as follows. The raw materials used were Ca-bentonite, coal ash, and activated carbon (as a pore-forming agent) at a 13:6:1 ratio. The raw materials were mixed with 20 vol.% water and 5 vol.% polyethylene glycol. Then, the samples were dried for 48 h at room temperature and at 105℃ to constant mass. Subsequently, the samples were heated according to a standard scheme (heating rate of 5℃/min for 1 h held at 1,100℃) in a medium-frequency vacuum induction furnace (Model ZGRS-160/2.55 Jinzhou Electric Furnace Co., Ltd., Jinzhou, China).

2.3. PTA wastewater

The PTA wastewater used in this study was obtained from a local PTA processing plant. The PTA wastewater had a chemical oxygen demand (COD) of 5,000–6,000 mg/L and total alkalinity (TA) of 1,000–1,500 mg/L. The feeding solution was prepared by diluting the PTA wastewater with different COD values. A 0.1% (v/v) microelement solution containing 50, 50, 30, 50, 50, 50, 50, and 50 mg/L H_3BO_3, $ZnCl_2$, $CuCl_2$, $MnSO_4{\cdot}H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $AlCl_3$, $CoCl_2{\cdot}6H_2O$, and $NiCl_2$, respectively was added.

2.4. Analytical methods

The COD, volatile suspended solids (VSS'), and pH were measured according to standard methods [19]. The PTA concentration was measured using a UV spectrophotometer (LAMBDA25, Perkin–Elmer, USA).

The structural analysis of the biofilm was conducted by scanning electron microscopy (SEM). The bio-beads samples were gently washed with a phosphate buffer solution and allowed to settle naturally. The bio-beads were then fixed with 2.5% glutaraldehyde in phosphate buffer and left undisturbed for 12 h. The fixed bio-beads were dehydrated with ethanol, dried in a bacteriological greenhouse at 35℃, and finally observed under a SEM system [20].

The porosity of the support was measured by the Archimedes method [21].

Biomass adhesion to the carrier particles was determined according to the method of Chen and Chen [22].

2.5. Experimental procedure

After the start-up period, the steady operation stage was initiated at an organic loading rate (OLR) of 7.3 kg COD/L. The OLR was progressively increased until the maximum rate value was reached. Throughout the entire procedure, the AFBRs were operated under four different operational conditions with varied COD values (2,500, 3,500, 5,000, and 6,000 mg/L) and HRTs (20, 15, 10, and 8 h), accordingly the liquid velocity (75, 100, 150, 180 L/h).

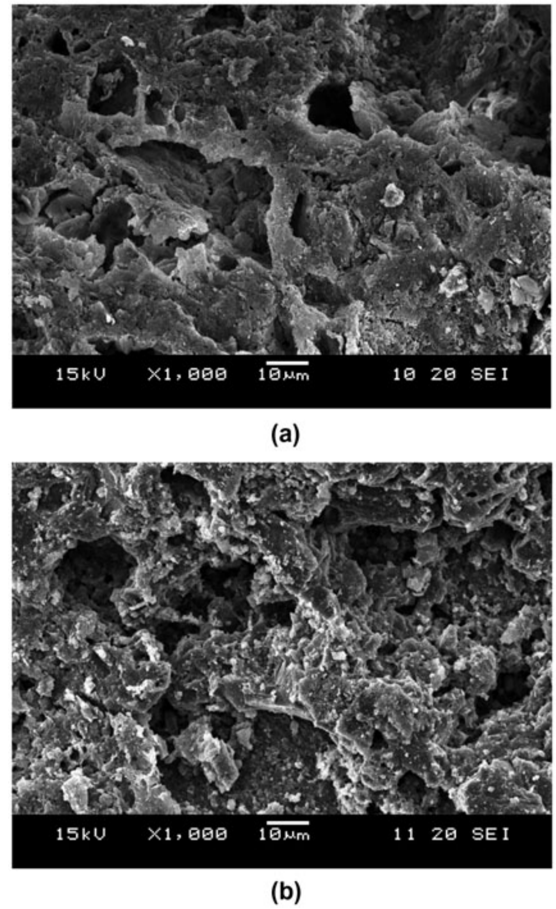


Fig. 2. SEM images of the (a) brick support and (b) porous ceramic support.

3. Results and discussion

3.1. Porous supports

The brick support exhibited 38.2% porosity, 2.13 g/cm^3 grain density, and 30–200 μm pore diameters. The brick beads used were 0.5–0.8 mm in diameter. The porous ceramic support exhibited 48.4% porosity, 1.96 g/cm^3 grain density, and 50–200 μm pore diameters. The porous ceramic beads used were 0.4–0.8 mm in diameter. Fig. 2 shows the SEM images of the brick support and porous ceramic.

3.2. Microbial community

The colonization of the microorganisms on the surface of the two supports was observed by SEM. Fig. 3 (a) and (b) show that no microorganisms were fixed on the surface of both supports because of the strenuous collision of the beads under fast fluidization. Thus, bacterial colonization on the surface was prevented.

In *R*1, the amount of biomass adhering to the brick beads was 9.3 mg VSS/g after a 34 d start-up period. By contrast, in *R*2, the amount of biomass adhering to the porous ceramic reached 13.5 mg VSS/g after an 18 d start-up period. Anaerobic bacteria showed a good affinity for immobilization on the interior of both supports (Fig. 4(a) and (b)). Highly dense microbial mass and very short start-up time intervals can be achieved using the two supports. Results showed that the attached microorganisms secrete the polysaccharide materials which hold the microorganisms together. The polysaccharide materials secreted by microorganisms possess high absorptive properties which allow biofilm microorganisms to grow in the interior of supports. Support surface properties are important in initial biofilm formation, the support with a porous microstructure and large specific area was highly suitable for bacterial retention. The better performance

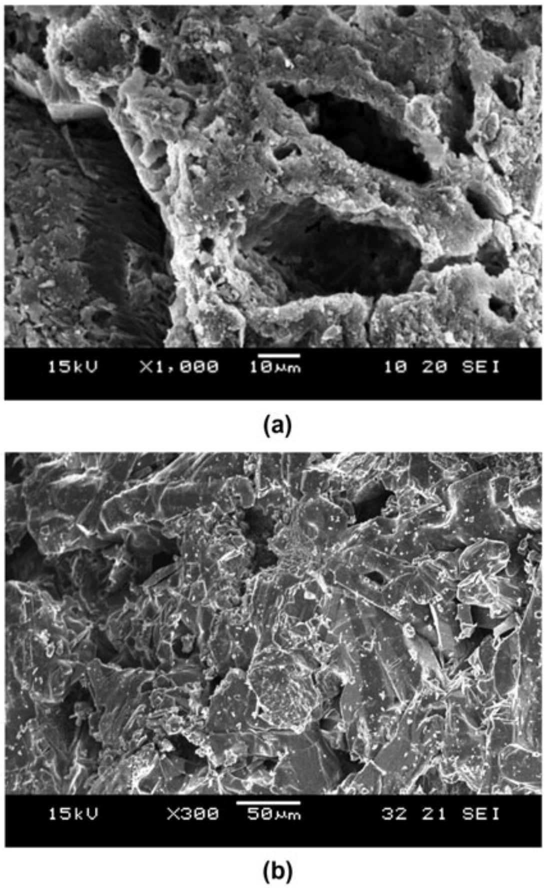


Fig. 3. SEM images of the (a) brick bead surface and (b) porous ceramic surface.

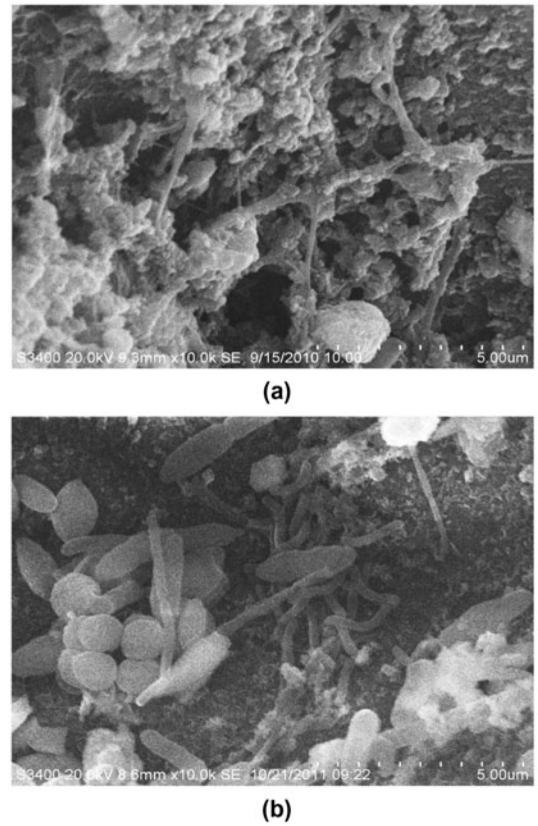


Fig. 4. SEM images of biomass attached to the (a) brick bead interior and (b) porous ceramic interior.

of *R*2 can be attributed to the characteristics of this support medium, including higher porosity (48.4%) than brick (38.2%) and larger pore diameter. The porous ceramic particles also had more creviced surfaces than the brick beads, and these crevices protected the developing biofilms from shear forces. Consequently, the biomass hold-up colonization was more uniform in the porous ceramic.

3.3. Start-up period

Considering the liquid velocity and bed expansion, a support amount equal to 35% of the active volume was deemed sufficient for obtaining adequate contact between the microorganisms and wastewater at a low energy cost. A secure space at the bottom of the reactor was also included to avoid support loss.

In this period, both reactors were operated at a low OLR (4.3 kg COD/(m^3 d)) and a long HRT (28 h), which was sufficient for biomass acclimatization and growth. *R*1 and *R*2 effectively worked after only 34 and 18 d, respectively. During this period, the system COD and TA removal efficiencies increased from approximately 25–60% for both two reactors (Fig. 5). This result can be attributed to that more substrate could be transfered to the biofilm at higher fluid velocity, it more suitable for the biofilm growth. Each support medium also provided a large surface area for biofilm formation and growth.

3.4. Steady operation period

For both reactors, steady operation started with 7.37 kg COD/(m^3 d) OLR and 20 h HRT. During the 73 d steady period, the influent COD levels gradually increased from 2,500 to 6,000 mg/L, the OLR increased from 7.37 to 18.52 kg COD/(m^3 d), and the HRT decreased from 19 to 8 h.

Fig. 6 shows the time course of the treatment efficiencies throughout the entire experimental period. *R*1 required 10 d to achieve a COD removal efficiency of 60% and a TA removal efficiency of 55% after start-up. *R*1 operation was stable during the 80 d steady

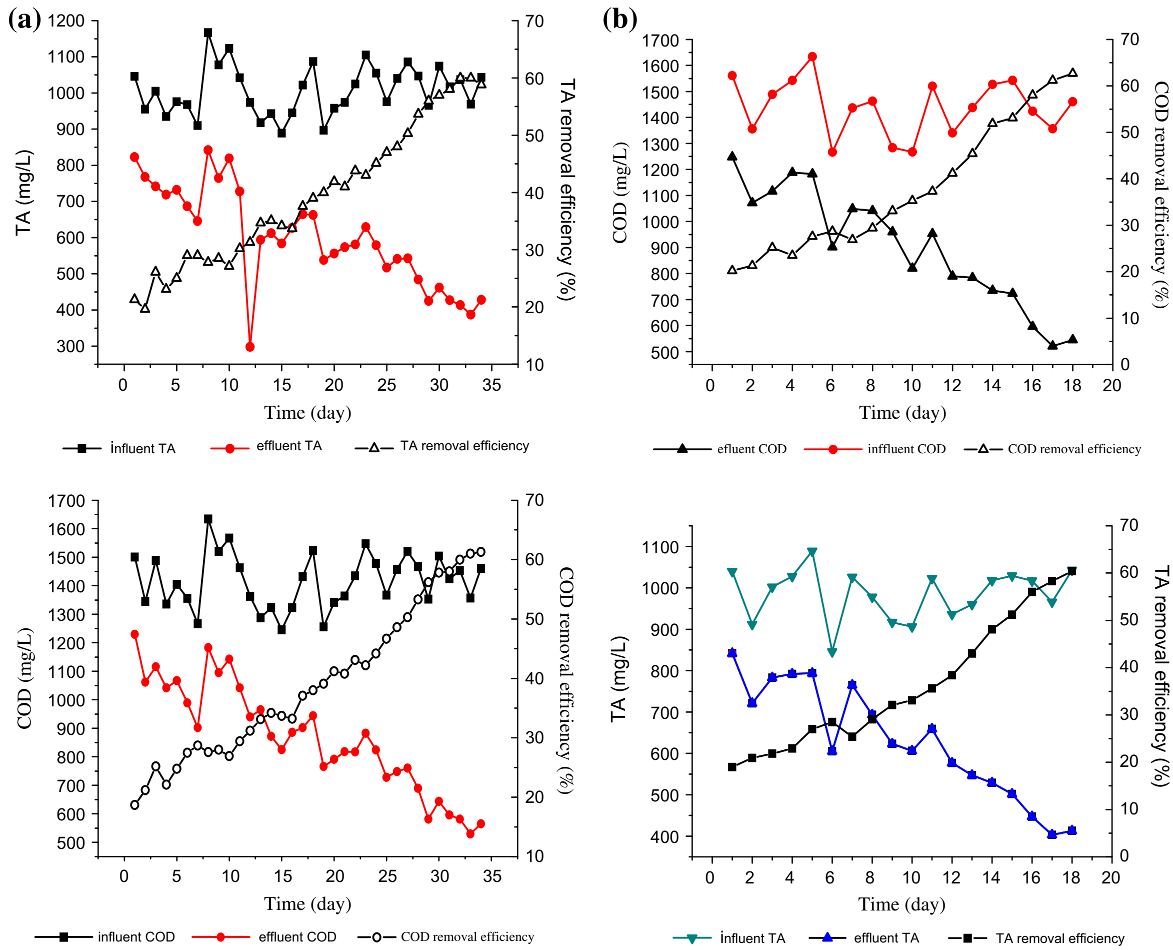


Fig. 5. Performance of (a) *R*1 and (b) *R*2 during the start-up period.

operation period, with increased influent COD levels. The COD removal efficiency was 65–75% and the TA removal efficiency was 60–70%. After 50 d, a high COD removal efficiency of 75% and a high TA removal efficiency of 70% were obtained and maintained during the entire stage 3, and the OLR was 12 kg COD/(m^3 d).

*R*2 needed 5 d to reach a COD removal efficiency of 64% and a TA removal efficiency of 58% after the start-up period. During the entire period, the COD removal efficiency was stable at 75–88%, and the TA removal efficiency was stable at 72–80%. The highest COD removal efficiency of 88% and the highest TA removal efficiency of 75% were also obtained at stage 3. *R*2 performed better than *R*1 during the steady period. The better performance was due to the fact that the porous ceramics in *R*2 enabled the attainment of more active biomass hold-up, thereby promoting the system efficiency and stability. Consequently, an opportunity for higher OLRs and resistance to inhibitors was provided.

The low COD and TA removal efficiencies at the beginning of the steady operation were due to the reduction in HRT from 29 to 19 h. The bacteria were not acclimated to the shocked system OLR. In addition, the suspended bacteria were mostly washed out with increased liquid velocity. However, after a short acclimation phase, the COD and TA removal efficiencies increased and became stable at high values. These results demonstrated that the AFBRs required a short HRT to remove both TA and COD from the high concentration PTA wastewater. The system also showed high resistance to the shocked OLR. This finding can be attributed to the higher fluid velocities tend to decrease the equilibrium biofilm thickness, which favored more substrate can be transported from the bulk liquid to the biofilm surface at higher fluid velocities. Under these conditions, the biofilm could reach the optimum thickness required to degrade the TA.

Compared with other PTA wastewater anaerobic treatment systems (showed as Table 1), the rapid mass transfer AFBRs demonstrated a number of advantages,

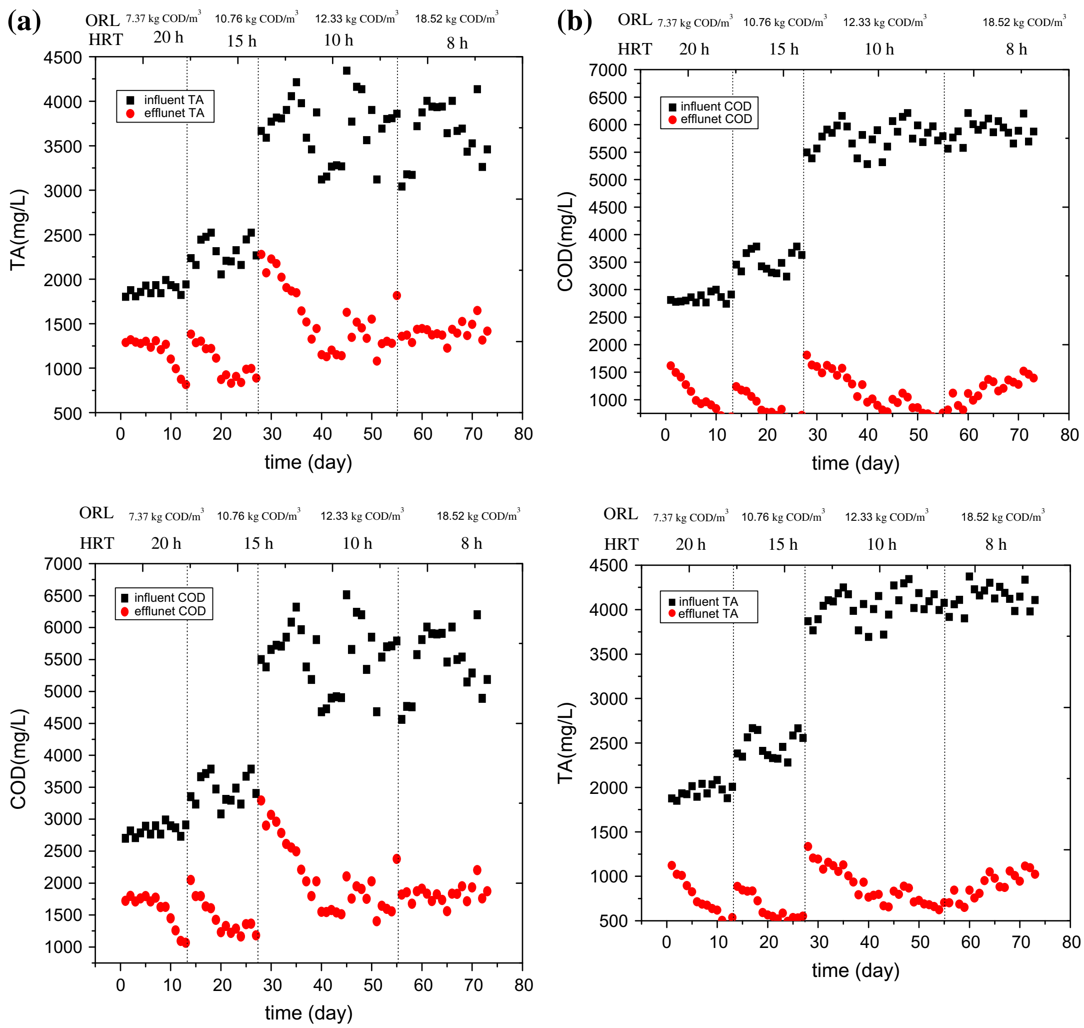


Fig. 6. Performance of (a) *R*1 and (b) *R*2 during the steady operation period.

including higher OLR, lower HRT, and stronger resistance against the concussive system OLR. These advantages are attributed to several design modifications made to improve system performance.

The support materials used in the AFBRs differed from the traditional low density support material. The density of the supports used in this study was much higher than the density of water. In the AFBRs, the high-density support particles and wastewater both flowed upward in the up-flow area at a higher fluidized velocity. However, they rapidly subsided under gravity in the down-flow area because of the high

Table 1
Performance of different anaerobic systems treating PTA wastewater

Anaerobic systems	Influent COD (mg/L)	OLR (kg COD/m^3 d)	HRT	COD removal rate (%)	Reference
Continuous stirred-tank reactor	4,000	16	6 h	45	[10]
Anaerobic filter	–	5.05	50 h	79	[23]
Internal circulation anaerobic reactor	1,100–1,600	–	10 h	50	[24]
Anaerobic fixed film fixed bed reactor	5,000	4–5	24 h	62	[25]
Anaerobic sludge blanket reactor	–	2.6	3 d	46.4	[26]

density. Consequently, the particles homogeneously distributed in the entire reactor. The fast fluidization and violent particle–water collision increased the relative inter-phase turbulence intensity and inter-phase mass transfer. The working volume and treatment efficiency of the reactor also remarkably increased. When the system OLR was shocked, the fast inter-phase mass transfer favored the different concentration wastewater dilutions. This phenomenon benefited the microbial degradation and eliminated the negative effect of the shocked OLR on the system treatment efficiency.

4. Conclusion

Two different porous high density support materials (brick beads and porous ceramics) were successfully used in AFBR to treat TA wastewater with short start-up and high treatment efficiency. The carriers were distributed equally in the entire reactor under fluidization condition, and the working volume and treatment efficiencies of the reactor were significantly enhanced. The fast fluidization and high-density porous carriers increased the relative inter-phase turbulence intensity and inter-phase mass transfer of the system.

*R*2 was more suitable for treating TA wastewater. Apart from presenting a shorter start-up period of 18 d, *R*2 showed a higher amount of biomass adherence (13.5 mg VSS/g), reaching a higher treatment efficiency of COD removal efficiency (75–88%) and TA removal efficiency (72–84%) during the steady period. Based on these results, the higher performance of *R*2 was attributed to the higher porosity, larger pore diameter, and higher roughness of the porous ceramic particles. All these characteristics favored biomass attachment.

Acknowledgements

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