Treatment of petroleum refinery wastewater using a sequential anaerobic–aerobic moving-bed biofilm reactor system based on suspended ceramsite

Mang Lu, Li-Peng Gu and Wen-Hao Xu

ABSTRACT

In this study, a novel suspended ceramsite was prepared, which has high strength, optimum density (close to water), and high porosity. The ceramsite was used to feed a moving-bed biofilm reactor (MBBR) system with an anaerobic–aerobic (A/O) arrangement to treat petroleum refinery wastewater for simultaneous removal of chemical oxygen demand (COD) and ammonium. The hydraulic retention time (HRT) of the anaerobic–aerobic MBBR system was varied from 72 to 18 h. The anaerobic–aerobic system had a strong tolerance to shock loading. Compared with the professional emission standard of China, the effluent concentrations of COD and NH3-N in the system could satisfy grade I at HRTs of 72 and 36 h, and grade II at HRT of 18 h. The average sludge yield of the anaerobic reactor was estimated to be 0.0575 g suspended solid/g COD removed. This work demonstrated that the anaerobic–aerobic MBBR system using the suspended ceramsite as bio-carrier could be applied to achieving high wastewater treatment efficiency.

Key words | anaerobic, hydrocarbon, MBBR, wastewater

INTRODUCTION

Petroleum refinery wastewater (PRW) is waste effluent originating from industries primarily engaged in refining crude oil and manufacturing fuels, lubricants and petrochemical intermediates. The estimated average water consumption in processing a barrel of crude oil is 246–341 L of water (Alva-Argáez et al. 2013), which accounts for 0.4–1.6 times the volume of the processed crude oil (Coelho et al. 2013).

PRW is composed mainly of hydrocarbons along with many other toxic organic compounds. Discharge of contaminants from PRW poses a risk to the environment due to high chemical oxygen demand (COD) and the toxicity of individual components in the wastewater. Nowadays, the refinery industry faces a huge challenge in meeting increasingly stringent environmental standards.

During the past decades, various technologies have been developed for treating PRW including coagulation (Demirci et al. 1997), adsorption (El-Naas et al. 2009), chemical oxidation (Abdelwahab et al. 2009), and biological techniques (Rahman & Al-Malack 2006). In general, it is difficult to remove small suspended oil particles and dissolved elements by physical technologies alone. Large amounts of oxidants are required when treating large quantities of PRW by chemical oxidation (Guo & Al-Dahhan 2005). Besides, chemical treatments may produce hazardous sludge. Compared with physical and chemical processes, biological treatment of oily wastewater can be a cost-effective and environmentally friendly method, and more compatible with existing plant facilities and operation (Fakhru’l-Razi et al. 2009).

The hydrolysis/acidification process has the following advantages (Wang et al. 2008): (1) the refractory organic substance is greatly reduced, hydrolyzed and acidified, and the sludge produced in the subsequent process can be largely decreased; (2) the biodegradability of the wastewater and the degrading rate of refractory pollutants can be improved; (3) it greatly reduces the operating cost, construction cost and facility area.

On the basis of conventional activated sludge (AS) process and fluidized-bed reactor, the moving-bed biofilm reactor (MBBR) was developed about 30 years ago and it has become popular in Europe (Trapani et al. 2010). The MBBR has been devised to offer the advantages of the biofilm system (compact, stable removal efficiency and simplicity of operation) without its limitations (medium channeling and...
clogging (Delnavaz et al. 2010). Although the MBBR system has been successfully applied for treating a wide variety of wastewaters (Trapani et al. 2010), there is less information on treatment of PRW using a two-stage MBBR.

The objective of the present study was to evaluate the treatability of PRW by using a sequential anaerobic–aerobic (A/O) MBBR reactor system where a porous suspended ceramsite was used as bio-carrier.

**MATERIALS AND METHODS**

**Preparation of porous suspended ceramsite**

The preparation process of the porous suspended ceramsite consists of slurry preparation, foaming, molding, drying, and calcination, which was performed according to Sepulveda et al. (2000) with some modifications. Briefly, six raw materials including fly ash, feldspar, calcite, fired tacle and kaolin were crushed, ground, and sieved through a 230-mesh sieve, respectively. Subsequently, 60 g fly ash, 18 g feldspar, 2 g calcite, 5 g fired tacle and 15 g kaolin were added to 50 mL deionized water to produce a slurry. Meanwhile, a mixture of 0.5 g Na2SO4 and 0.5 g MgCO3, which served as foaming agents, was added to the slurry. After homogenization, the slurry was cast into moulds. The sample was dried at 150 °C, and then calcined in a gas furnace at 1,260 °C for 2 h with heating rate of 50 °C/min. The calcined product was gradually cooled down to about 200 °C by natural ventilation, and then taken out of the furnace until cooling down to ambient temperature. The porous suspended ceramsite was finally obtained.

**Petroleum refinery wastewater**

The PRW was obtained from a Refinery in China. Raw effluent samples (not exposed to any prior treatment) were collected in a plastic container at the inlet point to the pre-treatment unit. To avoid composition change through photolysis or biological activities, the PRW-containing plastic container was immediately transported to the laboratory in an ice box and stored at 4 °C until required. Characteristics of the PRW sample are listed in Table 1.

**Experimental arrangement**

An MBBR system with an anaerobic–aerobic arrangement, as shown in Figure 1, was used to remediate PRW. The anaerobic reactor was a cylinder with an inside diameter of 9 cm and a working volume of 4.0 L, and the filling of the bio-carrier was approximately 50% (v/v). The aerobic reactor was rectangular with a working volume of 2.0 L, and the filling of the bio-carrier was about 50% (v/v). The hydraulic retention time (HRT) of the anaerobic MBBR was kept as half of that of the aerobic MBBR because the two reactors were connected in series and the filling ratios of the bio-carriers were identical. The raw PRW was pumped by a peristaltic pump into the anaerobic MBBR from the bottom. The influent was degraded by anaerobic microorganisms and the effluent was clarified in the settler. Then the supernatant flowed into the aerobic reactor, and then the effluent was overflowed out of the reactor. To maintain anaerobic conditions, the anaerobic MBBR was provided with a cover, and nitrogen was bubbled into both the reactor and the raw wastewater tank to inhibit access of air.

The bio-carrier shown in Figure 1 had an outside diameter of 12.5 mm, and a density of 0.98 g/cm³. The bulk density of the ceramsite would be close to that of water after biofilm growth, therefore only gentle agitation or aeration was required to obtain good carrier expansion.

**Operating procedure**

Fresh anaerobic and aerobic ASs, obtained from a refinery wastewater treatment plant, were used to feed the anaerobic and aerobic MBBR at the concentrations of 7 and 3 g/L mixed liquor suspended solids (MLSS), respectively. After inoculation, PRW was introduced into the two reactors to obtain their respective working volume, and continuous mechanical stirring or aeration was provided for the anaerobic or aerobic reactor, respectively. After 3 d of operation, one-half of the mixed liquid was drained off and then the same volume PRW was introduced to the anaerobic and aerobic MBBR respectively, for the next 3 d of the operation. This procedure was repeated eight times (24 d) to enhance the sludge activity and to prompt the growth of the biofilm.

### Table 1 | Values of the wastewater parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Level I criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.4–7.5</td>
<td>6–9</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>675–742</td>
<td>100</td>
</tr>
<tr>
<td>5-day biological oxygen demand (BOD₅)</td>
<td>318–373</td>
<td>30</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>42–48</td>
<td>10</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>31–35</td>
<td>15</td>
</tr>
<tr>
<td>Total suspended solids (TSS)</td>
<td>136–144</td>
<td>70</td>
</tr>
</tbody>
</table>

*Note: Integrated wastewater discharge standard of China; parameters except for pH are in mg/L.*
After that, the feed mode of wastewater was changed into continuous flow mode during a period of 124 d.

According to the influent flow rate, the operation time was divided into three stages as listed in Table 2. All laboratory experiments were performed at room temperature and dissolved oxygen (DO) concentration was controlled above 3 mg/L during the operation by regulating the aeration rate. The reactors were covered in order to minimize stripping and evaporation.

**Analytical methods**

DO, pH, and temperature were monitored *in situ* daily using portable devices. Water samples were filtered (0.22 μm) and then analyzed according to standard methods (State Environmental Protection Administration of China 2002). Briefly, COD was determined by titrimetric method after dichromate closed reflux. BOD₅ was measured via the oxygen consumption of bacteria breaking down organic matter in the sample over a 5-day period under standardized conditions. NH₃-N was determined by Nessler’s reagent colorimetry. Oil and grease was determined by using an infrared spectrophotometry oil-measuring instrument (H3-OCMA-350, Japan). Organic pollutants were detected by an Agilent7890-5975c gas chromatograph–mass spectrometer (GC/MS) equipped with an Agilent HP-5MS fused silica capillary column (60 m × 0.25 mm × 0.25 μm). The chromatography conditions were described elsewhere (Lu & Wei 2011).

The volatile fatty acids (VFA) concentration was analyzed by bicarbonate alkalinity and the acidification efficiency (AE) was calculated according to Zhang *et al.* (2010):

\[
AE = \frac{\text{VFA}_e - \text{VFA}_i}{\text{COD}_i} \times 100\%
\]

where VFAₑ and VFAᵢ were the VFA concentration present in the effluent and influent of the anaerobic reactor, respectively. CODᵢ was the COD concentration in the influent of the anaerobic reactor.

**Microbial analyses**

The toxicity of wastewater samples was determined using the Microtox® bioassay mentioned by Robidoux *et al.* (2004). In brief, water samples were filtered through a 0.22 μm Millipore filter to obtain filtrate. Aliquots (20 μL) of the bacterial reagent (*Photobacterium phosphoreum*) were added to a series of dilutions of filtrates. The salinity of the samples was adjusted to 2% with reagent-grade NaCl. The luminescence of bacteria was measured after 15 min of exposure at 15 °C, using a SDI M500 analyzer (SDI, USA). Microtoxicity values were the average of five replicates of each filtrate sample, expressed as EC₅₀ which was defined as the effective nominal concentration of elutriate (volume per cent) that reduces the intensity of light emission by 50%.

The biomass attached on the ceramsite was first desquamated by ultrasonic vibration for 20 min, and then the

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**Table 2 | Experimental conditions for the continuous flow process**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Operational days</th>
<th>HRT (h)</th>
<th>Anaerobic unit</th>
<th>Aerobic unit</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1 – 18</td>
<td>48</td>
<td>24</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>19 – 66</td>
<td>24</td>
<td>12</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>67 – 124</td>
<td>12</td>
<td>6</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>
mixed liquid was filtered through a 0.45 μm Millipore filter and dried at 105 °C for measurement of dry weight. The results were expressed as g suspended solid (SS)/L.

In this study, the data are presented in terms of arithmetic averages of three replicates values ± standard deviation.

**RESULTS AND DISCUSSION**

**COD removal**

The removal of COD in the anaerobic-aerobic MBBR system is shown in Figure 2. Stage I was considered as an unstable operation or start-up step to acclimatize microbes to the continuous flow. As the feed proceeded, the effluent COD of the anaerobic and aerobic MBBR decreased (Figure 2(a)) and the COD removal efficiency of the total system gradually increased (Figure 2(b)). On day 8, the total COD removal efficiency of the system reached 82.6%, indicating that the anaerobic-aerobic MBBR system had successfully completed start-up.

In this study, the anaerobic reactor served as a hydrolysis/acidiﬁcation system. It has been reported that the anaerobic hydrolysis/acidiﬁcation process is an effective pretreatment for the subsequent aerobic remediation of wastewater (Zhu & Chen 2003). Stages II and III can be considered as organic loading shock steps. At these two stages, the HRT of anaerobic MBBR was decreased from 48 to 24 h first, and then to 12 h, which caused an increase of organic loading rate (OLR) from 1.44 to 2.90 first, and then to 5.78 kg COD/(m² d). It can be seen from the experimental results that the HRT had a signiﬁcant effect on the performance of the MBBR. At day 8, the effluent COD of the anaerobic MBBR decreased to the level of 436 mg/L, which resulted in 37.7% of COD removal. The COD removal of anaerobic MBBR was kept stable when the HRT of anaerobic MBBR decreased from 48 to 24 h. When the anaerobic HRT decreased further from 24 to 12 h, the COD removal of anaerobic MBBR decreased signiﬁcantly, indicating that high OLR results in lower organic removal percentage. At HRT 48, 24 and 12 h, the average COD removal efﬁciencies in the anaerobic reactor were 35.8, 33.6 and 25.3%, respectively.

Figure 2(c) shows the relationship between AE and HRT during treatment. The AE increased gradually with time, indicating the growth of acidogenic bacteria in the anaerobic reactor. In general, greater AE corresponded to higher COD removal. The maximum AE was observed at HRT
24 h. A short HRT (12 h) would result in a reduction in the AE, due to the incomplete hydrolysis of the refractory organics at shorter HRT (Guerrero et al. 1999).

It can be found that the COD removal efficiency of aerobic MBBR was significantly higher than that of the anaerobic MBBR. With aerobic HRT decreasing from 12 to 6 h, the efficiency of the aerobic reactor was not influenced significantly. At HRT 24, 12 and 6 h, the average COD removal efficiencies in the aerobic reactor were 51.6, 53.3 and 50.4%, respectively. This indicated that the aerobic reactor had a greater ability than the anaerobic unit to resist organic shock loading. At total HRT of 72 and 36 h, the COD of aerobic effluent could satisfy the professional emission standard (grade I) (COD <100 mg/L) of China. The results indicated that the anaerobic–aerobic MBBR can effectively treat PRW to satisfy the government regulatory requirement. In the anaerobic–aerobic MBBR system, the aerobic reactor played a major role in COD removal, and the anaerobic MBBR was established to polish the treatment efficiency and ensure the supply of high quality effluent.

Moreover, the high concentration of biomass accumulated in the reactor due to the immobilization of the bio-carrier cannot be neglected. When the feed OLR was increased from 1.44 (72 h HRT) to 2.90 (36 h HRT) kg COD/(m³ d), the attached biomass was increased from 7.55 to 16.35 and from 13.46 to 27.62 g SS/L in the anaerobic and aerobic reactor, respectively (data not shown). In addition, the completely mixed operation mode of MBBR can make sludge, biomass and pollutants well contacted and less diffusion limitation, benefiting COD removal.

**COD balance and sludge yield in the anaerobic MBBR**

During anaerobic digestion, the production of methane is related to the COD reduction (McCarty & Smith 1986). Except for producing methane, the remaining portion of the reduced COD can be deemed as synthesis of biomass. This method has been used to estimate the sludge yield during the digestion of some fatty acids (Chen et al. 2008).

In this study, the biogas was collected by displacement of 2% NaOH solution to eliminate the CO₂; N₂ was neglected due to its content being less than 1%. In general, 1 g of methane was equivalent to 4 g of COD, and its volume was 1.4 L at standard temperature and pressure. Thus, the volumetric methane production rate (VMPR) could be calculated from the produced methane volume over the reactor volume and HRT.

Figure 3 shows that the VMPRs increase linearly with the OLR removed at a slope of 0.9355. As an average, 91.95% of the COD removed was converted to methane, and the remaining 8.05% was presumably converted to biomass. COD equivalence of the biomass in reactors is 1.4 g COD/g SS, based on an approximate formula for biomass (C₅H₇NO₂). Thus, the sludge yield was estimated to be 0.0575 g SS/g COD_removed, which was similar to 0.054 g SS/g COD_removed for VFAs (Fang et al. 1995) calculated using the same method.

**NH₃-N removal**

The feed ammonium concentration was 31–35 mg/L (Table 1). The time course of NH₃-N removed is plotted in Figure 4. It can be seen from Figure 4 that HRT had a small effect on ammonium removal. When the HRT of the combined system was 36 or 72 h, the total ammonium...
removal efficiency was consistently above 85%, and the final effluent ammonium concentration was 6.5–7.3 mg/L. In the anaerobic–aerobic MBBR system, the aerobic MBBR acted as the main undertaker for the NH₃-N removal, contributing to the total ammonium removal of about 74–83%, and the average removal efficiency was 78%. When the HRT of the aerobic MBBR was 6 h, the total ammonium efficiency slightly dropped to about 80%.

During wastewater treatment, ammonia can be eliminated in three ways: (a) assimilation into biomass; (b) ammonia volatilization; and (c) biological nitrification under aerobic conditions and denitrification process under anaerobic or anoxic conditions (Gálvez et al. 2005). In the aerobic MBBR, ammonia volatilization may be really low, considering the pH (7.3) for which NH₄⁺ (less volatile) predominated. In addition, biological nitrification could occur in the aerobic reactor, resulting in the removal of ammonia.

The loss of ammonium in the anaerobic reactor may be attributed to the utilization of NH₃-N by anaerobic microbial assimilation. To prove this explanation, an approximation procedure was performed as follows. Assuming that the average COD removal in the anaerobic reactor was 240 mg/L and the sludge yield was 0.0575 g SS/g CODremoved, the synthesized biomass can be evaluated as 13.8 mg SS/L; and an approximate formula for biomass is C₅H₇NO₂, so the required nitrogen for biomass synthesis was 1.7 mg/L. The ammonium concentration in the feed was around 30 mg/L, so the theoretical ammonium removal efficiency was about 5.5%, which was in agreement with the observed removal efficiency.

In this study, pH was continuously monitored. It was found that the influent pH of aerobic reactor was stable at around 7.3, and the effluent pH was kept at 7.1. The pH was within the range required for good biodegradation. Thus, no pH adjustment was performed in this study.

**Microtoxicity**

Refined information on the changes in wastewater quality undergoing treatment can be obtained by Microtoxicity assessment. Microtox analysis was conducted on the 15th, 45th and 90th day, to monitor toxicity levels of the treated PRW. It can be found from Figure 5 that the acute toxicity of PRW to the bacterium *Photobacterium phosphoreum* decreased greatly after flowing through both anaerobic and aerobic MBBR. However, as the total HRT decreased from 36 to 18 h, the reduction in the toxicity of treated wastewater declined. This may be due to the lesser extent of biodegradation of some toxic intermediates under high HRT conditions.

**Comparison with conventional activated sludge process**

To verify the advantages of the MBBR, the PRW was treated using a conventional AS system. The AS system had the same configuration as the MBBR system; the only difference was that there was no bio-carrier in the AS reactor. The AS process was performed under the same experimental conditions as set for the MBBR treatment. Table 3 lists the average removal efficiencies of COD and NH₃ in the AS and MBBR systems at different HRTs. As shown, at low OLR (72 h HRT), MBBR and AS systems showed nearly comparable performances in COD and NH₃ removal. However, the performance difference between the two systems was enlarged as a function of increasing HRT. These results demonstrated that the MBBR system had higher resistance to organic shock loading than the AS systems.

<table>
<thead>
<tr>
<th>HRT (h)</th>
<th>COD (%)</th>
<th>NH₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>82.5</td>
<td>86.2</td>
</tr>
<tr>
<td>36</td>
<td>77.4</td>
<td>80.6</td>
</tr>
<tr>
<td>18</td>
<td>68.3</td>
<td>65.5</td>
</tr>
</tbody>
</table>

*Table 3 Comparison of MBBR system with activated sludge treatment*
Degradation of refractory organics

The GC/MS results of the feed and the effluent from the MBBR processes at day 48 are listed in Table 4. The numbers of certain organics (including phenols, ketones, esters, amines and ethanols) increased in the anaerobic reactor, which may be attributed to the anaerobic degradation of organics.

Table 5 also lists the concentrations of 16 priority polycyclic aromatic hydrocarbons (PAHs) in the streams of the MBBR and AS systems. As far as the MBBR process is concerned, Nap, Fle, Phe, and Ant were the four dominant constituents, representing 11.7, 21.3, 28.4 and 10.6% of the total 16 PAHs detected in the influent. Their respective removal efficiencies were 38.3, 45.7, 38.8 and 32.3% for the anaerobic MBBR reactor, and 77.5, 81.6, 68.9 and 81.4% for the aerobic MBBR reactor. The removal efficiency of the 16 PAHs was 39.4 and 74.6% for the anaerobic and aerobic MBBR reactor, respectively. Moreover, it can be seen from Table 5 that the concentrations of individual PAHs were slightly lower in the MBBR reactors than in the AS reactors, indicating that the MBBR system had higher capability of degrading PAHs than the AS system.

It has been demonstrated that a number of hydrocarbons including PAHs could be degraded anaerobically (Chang et al. 2002). After aerobic degradation, the numbers of certain organics decreased markedly, indicating that the aerobic process was efficient in removing refractory organics.

CONCLUSIONS

This study demonstrated that the MBBR filled with the suspended ceramsite as bio-carrier with an anaerobic and aerobic arrangement was an effective and feasible approach for simultaneous removal of COD and ammonium from PRW. Results showed that the total COD and NH3-N removal efficiencies were higher than 85%, at 72 and 36 h HRT. Compared with the professional emission standard of China, the effluent concentrations of COD and NH3-N in the integrated system could satisfy grade I (COD < 100 mg/L, NH3-N < 15 mg/L) at HRT of 72 and 36 h, and grade II (COD < 120 mg/L, NH3-N < 25 mg/L) at HRT of 18 h. The sludge yield of the anaerobic MBBR was estimated to be 0.0575 g SS/g COD removed from the relation of VMPR and organic loading removed. High accumulations of biomass in the ceramsite ensured the high treatment capacity and operational stability, making the MBBR process attractive.

ACKNOWLEDGEMENT

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