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Assessing the treatment of acetaminophen-contaminated brewery wastewater by an anaerobic packed-bed reactor

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Abstract

The treatment of high-strength organic brewery wastewater with added acetaminophen (AAP) by an anaerobic digester was investigated. An anaerobic packed-bed reactor (APBR) was operated as a continuous process with an organic loading rate of 1.5-g COD per litre per day and a hydraulic retention time of three days. The results of steady-state analysis showed that the greatest APBR performances for removing COD and TOC were as high as 98 and

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93%, respectively, even though the anaerobic digestibility after adding the different AAP concentrations of 5, 10 and 15 mg L^{-1} into brewery wastewater can affect the efficiency of organic matter removal. The average CH_4 production decreased from 81 to 72% is counterbalanced by the increased CO_2 production from 11 to 20% before and after the injection of AAP, respectively. The empirical kinetic models for substrate utilisation and CH_4 production were used to predict that, under unfavourable conditions, the performance of the APBR treatment process is able to remove COD with an efficiency of only 6.8%.

Keywords: acetaminophen-contaminated brewery wastewater; anaerobic packed-bed reactor; kinetic model; methane production; substrate utilisation.

1. Introduction

Pharmaceutical industry wastewater may contain high-value active ingredients, such as acetaminophen, which is classified as recalcitrant because of its physiological storage behaviour. Pharmaceutically active compounds (PACs) present in wastewater can affect the biodiversity and ecology of the receiving waters when released without treatment (Jones et al., 2004; Mendoza et al., 2015). The occurrence and persistence of PACs and their metabolites have been detected in sewage treatment plant effluents, surface waters, and, less frequently, in ground water and drinking water even though the selection and control of a safe and effective therapeutic dose in human and veterinary practices can be made (Sun et al., 2014; Tambosi et al., 2010). The bacterial toxicity of PACs may play an important role in decreasing the performance of biodegradable organic matter removal in affected treatment systems (Sponza and Demirden, 2007). Acetaminophen, or paracetamol (N-acetyl-4-aminophenol) (AAP), is the most frequently used analgesic and antipyretic drug (Narang et al., 2015). In the European Union, sewage treatment effluents were identified as the point source of active ingredients in the river water, with AAP concentrations up to 6 μg L^{-1}, even though more than 65 μg L^{-1} of AAP was reported in the Tyne River, UK (Duran et al., 2011). The presence of PACs, such as the analgesic AAP in natural waters, has been detected at concentrations of 10 μg L^{-1} in the USA (Kolpin et al., 2002). PACs can be classified as newly emerging pollutants (NEPs) (Bell et al., 2011; Murray et al., 2010; Zenker et al., 2014) and may cause subtle effects on aquatic and terrestrial organisms due to their virtual ubiquity in various environments (Kummerer, 2011; Zuccato et al., 2006). Among the major categories of NEPs are pharmaceuticals and illicit drugs, steroid oestrogens (hormones and contraceptives) and personal care products (Mostafa et al., 1990; Nikolaou, 2013; Ramachandran and Saraswathy, 2014). Therefore, the effectiveness of biological and physical treatment processes in the removal of pharmaceuticals and other organic compounds needs to be verified (Galhetas et al., 2014; Stackelberg et al., 2007; Yoon and Byun, 2013; Zaib et al., 2013).

Wastewaters of pharmaceutical industries generally contain high organic loads, and treatment is primarily conducted using two major types of aerobic and anaerobic digestion (Novak et al., 2003), even though it can be advanced by an alternating anoxic aerobic process to remove inorganic nitrogen pollution (Fulazzaky et al., 2015). Anaerobic digestion processes have been widely used for the treatment of high-strength industrial wastewaters containing herbicides, antibiotics, phenols, cosmetics, etc. (Abdullah et al., 2013; Chen et al., 2011). A hybrid bioreactor of hollow fibre microfilter membrane and cross-linked enzyme aggregates has been used for the elimination of AAP (Ba et al., 2014). Consequently, in this work, an anaerobic packed-bed reactor (APBR) is used to treat AAP-contaminated brewery wastewater due to the large packing media surface area available for the attachment of microorganisms and the reduced bioreaction time (Jong and Parry, 2003). The use of a membrane or combined membrane bioreactor could be useful for the treatment of synthetic pharmaceutical wastewater containing AAP or trace organic contaminants (Nguyen et al., 2013; Shariati et al., 2010). Cascaded anaerobic ponds are the most commonly used process for the treatment of wastewaters to withstand high organic loading rates, such as for palm oil mill effluent (Fulazzaky, 2013). High-rate anaerobic treatment of pharmaceutical wastewaters in a packed-bed biofilm reactor with the various types of supporting materials possesses a basic understanding of fixed-film biological reactor processes (Gullicks et al., 2011; Satya and Venkateswarlu, 2013). The materials used to retain active biomass in the reactor can be arranged in various confirmations made out of different materials, such as plastics, granular activated carbon, sand reticulated foam polymers, granite, quartz and stones, and can be loosely or modularly packed. The advantages of using the supporting materials as biofilm carriers are that they can assure a shorter start-up period and a greater amount of retained inoculum for faster start-up (Kim et al., 2004). APBR would be suitable for the treatment of high-strength wastewaters and has the traditional biofilm resistance to shock loading and biological inhibition (Scullion et al., 2007); this can be operated in either an up-flow or down-flow feed mode (Nandy and Kaul, 2001; Yu and Gu, 1996). Although the treatment of pharmaceutical wastewaters containing synthetic drugs by anaerobic digesters has been widely studied in the last two decades (de Graaff et al., 2011; Lin et al., 2012; Masse et al., 2000), the kinetic models of substrate utilisation and methane (CH_4) production in treating the AAP-contaminated wastewater by an APBR needs to be established to predict digester performance under unfavourable conditions. This may contribute to a better understanding of the application and effectiveness of the anaerobic digestion process for the removal of PACs from wastewaters.

The objectives of this study are as follows: (1) to assess the performance of APBR for the treatment of AAP-contaminated brewery wastewaters, (2) to monitor the fluxes of CH_4 and carbon dioxide (CO_2) from a small-scale anaerobic digester to the atmosphere, and (3) to investigate the kinetics of substrate utilisation and CH_4 production in an anaerobic digestion process for treating a high-strength organic wastewater under mesophilic temperature conditions.

2. Materials and Methods

2.1. Anaerobic packed-bed reactor

The APBR treatment system (dos Reis and Silva, 2014; Ferraz Jr et al., 2014; Singh and Prerna, 2009) used in this study consists of a 22.5-L cylindrical PVC bioreactor, 10-L raw wastewater storage tank, 0.5-L Schott bottle filled with AAP and 10-L effluent tank, as shown in Figure 1. The bioreactor filled with plastic-based packing media can treat the wastewater in an up-flow feed mode. The fragmented pieces of polyurethane pipe, with an inside diameter of 0.64 cm, outside diameter of 0.95 cm and density of 900 kg m^{-3}, were used as a matrix to immobilise microorganisms. The percentage of void space in the bioreactor was approximately 85%, with an effective volume of 18.5 L. The addition of AAP from the Schott bottle was regulated using a 230-V centrifugal water pump (Totton Pump Limited, Southampton, England) to allow the joining of it to the raw wastewater feeding the APBR. The fed wastewater enters the APBR treatment system through a downcomer tube of 0.6 L inside the cylindrical PVC bioreactor. The experimental set up used during this study was maintained at mesophilic conditions (37ºC), and thus the bioreactor sidewall was enclosed within the tubular PVC water-jacket connected to a heat exchanger. The circulations of fed wastewater and effluent were regulated using the centrifugal pumps, and thus the upflow velocity was 1.25 cm h^{-1}. The gas pipeline that has access to biogas production in the bioreactor was connected to an optical gas bubble counter (made in-house at Newcastle University, UK), giving a measurement of the gas volume. The biogas production was monitored and collected in the range of 0 to 1.5 L h^{-1}. The APBR treatment system was equipped with two sampling ports that allowed biological solids and liquid samples to be withdrawn periodically for quantitative analysis throughout the experiment.

(**Fig. 1** could be here)

2.2. Operating procedures

One litre of anaerobic granular sludge from an anaerobic sludge digester at the municipal wastewater treatment plant of Hexham town, Northumberland, UK, was used as the microbial inoculum for the start-up of the APBR treatment process. The brewery wastewaters (Scottish and Newcastle Breweries, Newcastle, UK) have an average chemical oxygen demand (COD) concentration of 88 g L^{-1}; therefore, the wastewater used was diluted to 5.68% of the original concentration with potable water to have an influent COD concentration of 5 g L^{-1}. The initial average mixed liquor volatile suspended solids (MLVSS) concentration in the APBR was appoximately 6 g L^{-1}. To assess the effect of AAP on the APBR performance, the Schott bottle was filled with the AAP of Calpol Six Plus 250-mg/5-mL Suspension. The inlet arrangement in the wastewater-fed APBR used a centrifugal pump control to achieve a desired concentration of AAP in the diluted brewery wastewaters. The anaerobic digestion system was operated at 37°C with an organic loading rate (OLR) of 1.5-g COD per L per day and a hydraulic retention time (HRT) of three days. The essential nutrients and trace elements were added and controlled to provide a balanced supply of nutrients with a COD : N : P ratio of 250 : 7 : 1 feeding the APBR for the most efficient bacterial growth (Jefferson et al., 2004; Méndez et al., 1989); therefore, it needs to verify the presence of N and P in the brewery wastewaters regularly before using it for feeding the reactor. The concentrations of COD and total organic carbon (TOC) at inlet and outlet of the bioreactor were monitored daily before and after the addition of AAP into the diluted brewery wastewaters. The performance of the APBR treatment system was monitored in terms of COD, TOC, CH_4 production and CH_4 yield to investigate how the presence of AAP affected the treatment of brewery wastewaters. Even though this study has not particularly focused on the effect of pH on the APBR performance, the pH was measured daily using a pH meter at inlet and outlet of the bioreactor. The inlet AAP concentration was selected in the range of 0 to15 mg L^{-1} based on the ecotoxicity EC_{50} information (Petrie et al., 2015) to understand if the degradation of organic matter (see COD, TOC) in the presence of AAP under anaerobic conditions would be effective. The experiments were run for four consecutive steps of 20, 10, 10 and 10 days by adding the inlet AAP concentrations of 0, 5, 10 and 15 mg L^{-1}, respectively, into the diluted brewery wastewaters, as shown in Table 1.

(**Table 1** could be here)

2.3. Analytical methods

In this study, the samples selected for the soluble COD measurement (see Standard Methods 5220-C) (APHA, 2005) were made of two liquids, i.e. (1) supernatant liquor after centrifugation to determine the MLVSS concentration in order to represent active microorganism mass in the bioreactor (Coskuner et al., 2005) and (2) fresh permeate coming out from the bioreactor. The measurements of volatile fatty acids (VFAs) were carried out for the liquid in bioreactor using gas liquid chromatography (Unicam 610 Series Gas Chromatograph with an auto-injector and a PU 4811 computing integrator) to having a rational understanding of acidogenesis. The percentage of CH_4 and CO_2 in the biogas was determined using gas chromatography (Becker Model 403 Gas Chromatograph with a Unicam 4815 Integrator). The APBR treatment system was operated for 50 days, and the CH_4 production profiles were monitored daily using an optical gas-bubble counter (Newcastle University, UK) having a measurement range of 0 to1.5 L h^{-1} and precision within ± 1%.

3. Results and Discussion

3.1. Reactor performance

Anaerobic treatment of high-strength brewery wastewater with an influent COD concentration of 5 g L^{-1} allowed the APBR treatment system to operate at an OLR of approximately 1.5-kg COD per m^3 per day with an HRT of three days. Figure 2 shows the variations of COD and TOC removal efficiency for the APBR treatment process under four different test conditions for 50 days of experiment. During the first stage of 18 days of the experiment, the efficiency of APBR in removing COD, having long enough to reach a perfect steady state, may range between 68 and 75%. Such an efficiency then increases to approximately 84% for two days at its real steady-state conditions during the 19th and 20th day of the experiment before the addition of AAP. For the remaining 30 days of the experimental run, the AAP concentrations of 5, 10 and 15 mg L^{-1} must be added to the brewery wastewater applicable to the APBR formation assays under different exposure conditions associated with toxicity of AAP to anaerobic bacteria for the second (10 days), third (10 days) and fourth stage (10 days) of conducting the experiment, respectively. With a low upflow velocity of 1.25 cm h^{-1}, even if each experiment of different amounts of added AAP has the chance to run for 10 days, anaerobic bacteria have had plenty of time to adapt to their environments and to have given rise to numerous descendant forms for removing organic matter from contaminated brewery wastewater.

(**Fig. 2** could be here)

For the first stage of 20 days, the use of APBR to remove TOC would likely increase the average efficiency step-by-step beginning from approximately 61% for eight days to 68% for three days to 89% for six days and finally to 93% at its perfect steady state for three days of the experiment. This describes how to reach steady-state operation in converting organic matter in a continuous mode seemingly matched with the bacterial growth phase (Arcury, 1982; Narihiro et al., 2004). Under steady-state conditions from the 12th to the 20th day of the experiment, the performance of APBR to remove COD would be much lower than that to remove TOC; it is only because of a strong proportion of non-oxidable organic compounds. Improved treatment efficiency of COD removed in the APBR as monitored by the highest CH_4 production of 89.3% (see Fig. 3a) upon the addition of 5 mg L^{-1} AAP can reach up to approximately 98% of its perfect steady state; however, the APBR performance to remove TOC was relatively stable with an efficiency of approximately 93%. The performance of the APBR treatment process after the addition of AAP with three successive concentrations of 5, 10 and 15 mg L^{-1} may be illustrated by monitoring the daily variations of COD and TOC efficiency. These variations in treatment system efficiency emerged even though the figure compared only these two parameters that shared similar environmental trend lines on a biochemical basis for the AAP-induced inhibition of methanogenic fermentation of brewery wastewaters; high variability in the zigzag lines on per cent removals of COD and TOC fortified with the addition of 10- and 15-mg L^{-1} AAP concentration for the third and fourth stages of conducting the experiment in contrast with the increasing trend of COD and TOC removal for the second stage, which contained an AAP concentration of 5 mg L^{-1}. These findings suggest that the addition of a low dose of AAP may have a biofilm resistance to shock loading and biological inhibition (Satya and Venkateswarlu, 2013) and avoids fluctuation in the rumen methanogenesis while having little adverse effect on rumen fermentation (Alidina et al., 2014; Patra and Yu, 2013). Some of the limitations of this study include the lack of assessing the APBR performance to remove AAP and of verifying the AAP removal mechanisms that occurred by either biosorption or biodegradation.

(**Fig. 3** could be here)

3.2. Biogas production

The use of the modified Gompertz model can be beneficial for performing better prediction regarding having a lower difference between the measured and predicted biogas yields (Bah et al., 2014). In this study, anaerobic digestion was performed as a continuous process of 1.25 cm h^{-1} upflow velocity, where organic matter was constantly added with an OLR of 1.5-g COD L^{-1} d^{-1} to the reactor. The end biogas products were monitored daily for 50 days. In an experimental campaign, the daily biogas production can be determined and would make direct comparisons possible between the percentages of CH_4 and CO_2; the samples of biogas were periodically analysed to evaluate percentages of CH_4, CO_2 and other gases, as shown in Figure 3a. Performance ratings would remain relatively stable over the experimental period, with a few exceptions. Irregular microbial CH_4 production by intermittent decrease in CH_4

percentage could be due to the high production of other biogases. High stresses resulting from the addition of AAP with a concentration of 5 mg L^{-1} in fed wastewater can reduce to 37.5% for extremely low CH_4 production at the 22-day experiment, even though the fraction of CH_4 production can increase after the community of microbes has already adapted to that background supply of AAP. There were no differences in CH_4 production in absolute terms between the treatments of AAP addition with concentrations of 10 and 15 mg L^{-1}, and the average CH_4 production of the APBR treatment process was approximately 72%. Four consecutive stages of anaerobic digestion are as follows: (1) hydrolysis: a chemical reaction where insoluble and complex soluble organics are converted into simple soluble organics, hydrolysed by extracellular enzymes (Zhang et al., 2007); (2) acidogenesis: a biochemical reaction where simple soluble organics are converted into volatile fatty acids; (3) acetogenesis: a biochemical reaction where volatile fatty acids are converted into acetic acid, CO_2 and H_2; and (4) methanogenesis: a biochemical reaction where acetates are converted into CH_4 and CO_2, while H_2 is consumed (Conrad, 1999). Figure 3a shows that the average CH_4 production decreased from 81% before to 72% after AAP injection of the concentrations of 10 and 15 mg L^{-1} which may be indicated if the acetogenesis of volatile fatty acids causes a marked increase in CO_2 production, which could result in the percentage of CO_2 production increasing from 11 to 20%. The effects of AAP, an inhibitor of methanogenesis, on microbial metabolism in sludge from a mesophilic (37°C) anaerobic digestion were found from the third and fourth step of the experiment, for which the CH_4 production was decreased by 9% (81 - 72%), which appears to be counterbalanced by an increased CO_2 production of 9% (20 - 11%), balancing the biogases (CO_2, CH_4, other gases) generated by anaerobic digestion released into the atmosphere with an emission of 100%. It is likely that the inhibition of methanogenesis by the injection of AAP with the concentrations of 10 and 15 mg L^{-1} affects the methanogenic degradation rates of the acetates (Zinder et al., 1984).

The oxidative transformation kinetics of AAP under different conditions have been investigated to understand the fate of AAP in natural systems (Tan et al., 2014; Xiao et al., 2013). The effects of adding AAP with different concentrations on VFA composition (Wong et al., 2008) in the bioreactor were investigated, as shown in Figure 3b, because it does have an influence on methane yield and methanogenic bacteria growth (Wang et al., 2009). As substrate composition and properties were changed by the addition of AAP with a concentration of 5 mg L^{-1} to increase the organic strength of brewery wastewaters, the presence of VFAs in the bioreactor increased step-by-step from approximately 0.89 g L^{-1} at the 20th day to 2.02 g L^{-1} at the 25th day of the experiment due to the first addition of 5-mg L^{-1} AAP can disturb the energetic level of the cells for bacterial growth and the balance of anabolic and catabolic reactions cannot be maintained. After the addition of 5-mg L^{-1} AAP, high VFA concentration of approximately 2.02 g L^{-1} verified from the 25th to the 27th day of the experiment (see Fig. 3b) can cause the pH to decrease from 5.39 to 4.99 (see Fig. 4) and results in toxic conditions in the bioreactor (Franke-Whittle et al., 2014), leading to lower CH_4 production from 89.3 to 60.4%. The pH (see Fig. 4) of approximately 9.6, except for the first 10 days of the experiment, at the inlet of the bioreactor could be higher than that of approximately 6.6 at the outlet of the bioreactor after the addition of 10- and 15-mg L^{-1} AAP. A significant change in the pH at the outlet of the bioreactor occurred during the adaptation of anaerobic bacteria to their environments from the 5th to the 9th day of the experiment before and from the 20th to the 24th day of the experiment after the addition of AAP would be due to metabolic instability can lead to a change in the concentration of H^+ ions (Crepaldi et al., 2010). During the development phases from the second to third and then to fourth stage of conducting the experiment, the anaerobic bacteria in the bioreactor adapted to the new wastewater characteristics imposed by the addition of AAP regardless of whether the OLR and HRT were unchangeable. The VFA concentration was monitored daily in the bioreactor indicating only minimal changes in methanogen numbers during periods of high VFAs and showing a decreasing trend over time, with the effects of increasing the AAP concentration in the fed wastewater on the VFA concentration not being clearly detected due to the absence of independent trend lines (Franke-Whittle et al., 2014). The decrease in VFA concentration from 0.59 g L^{-1} at the 30th day to 0.36 g L^{-1} at the 40th day of the experiment and from 0.36 g L^{-1} at the 40th day to 0.30 g L^{-1} at the 50th day of the experiment was verified after the addition of AAP with the concentrations of 10 and 15 mg L^{-1}, respectively (see Fig. 3b).

(**Fig. 4** could be here)

3.3. Methane production and methane yield

Under anaerobic conditions, anaerobes grow by fermentation or anaerobic respiration, in which the daily CH_4 production can be monitored across a variety of experimental conditions. With increasing pressure to treat wastewater effectively, the potential of CH_4 production from anaerobic digestion would represent one of the most important routes towards reaching renewable energy targets (Olsson and Fallde, 2015). Among valorisation possibilities, anaerobic digestion for CH_4 generation appears to be the most technically feasible to not only be environmentally friendly but also profitable (Ruiz and Flotats, 2014). In this study, even though the production of CH_4 gas from the breakdown of organic matters contained in brewery wastewaters can move in a zigzag manner during the treatment process of 50 days, this would have resulted in increased CH_4 production, with its maximum of 15.7 L d^{-1} being achieved with a fed AAP concentration of 15 mg L^{-1} during the 48-day experiment (see Fig. 5). The sensitivity of AAP with a concentration of 5 mg L^{-1} to the variations of CH_4

production in the APBR treatment system can have greater differences than those with the concentrations of 10 and 15 mg L^{-1} due to the change of wastewater characteristics, which immediately contribute to shock loading (Scullion et al., 2007) and affect microbial activity and CH_4 production during the methanogenic stage of anaerobic digestion in the second stage of the experiment. The average CH_4 production during the treatment process was 8.5 L d^{-1}, although the daily variation was up to more than fifteen times higher when comparing CH_4 production at the end of the 50-day experiment (i.e. 15.2 CH_4 L d^{-1}) with that of the first day of the experiment (i.e. 0.9 CH_4 L d^{-1}). Methane yield is defined as the amount of CH_4 produced for a given quantity of organic matter (see COD) that is removed and can indicate the performance of the metabolic activity of a methanogenic ecosystem (Michaud et al., 2005; Seppälä et al., 2009). The extent of CH_4 production depends primarily on the quantity of degradable organic matters in the brewery wastewater, the temperature, and the design and operating features of the APBR treatment system. The results of the potential of CH_4 production per kg of COD removed showed that fermentation of waste and organic substrates from the AAP-contaminated brewery wastewaters under mesophilic conditions of 37^{o}C at a three-day HRT might achieve the highest CH_4 yield of 0.35, regardless of fluctuating CH_4 production (see Fig. 5). The mechanism behind the increased CH_4 production could be dependent on the biochemical reactions during the bacterial methanogenesis, and the fractionation yielded closely approached the thermodynamic equilibrium between CO_2 and CH_4 (Botz et al., 1996). The addition of AAP with the concentrations of 5, 10 and 15 mg L^{-1} to the brewery wastewaters essentially accelerated the CH_4 production and remained stable throughout the life of the experiment. The increase in CH_4 yield could be attributed to the addition of AAP into the feed regime particularly at the AAP concentrations of 10 and 15 mg L^{-1}.

(**Fig. 5** could be here)

3.4. Empirical kinetic models for substrate utilisation and methane production

In this work, the applicability of the empirical kinetic models (Barthakur et al., 1991; Fulazzaky et al., 2013a; Málek and Criado, 1992) in substrate utilisation and CH_4 production analysis can be discussed after the addition of AAP in the fed wastewater. Under steady-state conditions, the substrate removal rate (see the COD removal rate) can be obtained from the equation of $r = (C_o - C_s)/\theta$, where r is the COD removal rate (in g L^{-1} d^{-1}), C_o is the influent COD concentration (in g L^{-1}), C_s is the effluent COD concentration (in g L^{-1}) and θ is the HRT (in d) (Borja et al., 2003). Note that $C = C_o - C_s$ is defined as the removed COD concentration during the treatment process (in g L^{-1}). This allows the direct calculation of r as the substrate removal and the CH_4 production progress throughout the treatment process based on the data from monitoring the influent and effluent COD concentrations. A plot (Fig. 6; see curve-1) of r versus C can determine the linear regression model equation to represent the experimental data in the form of $r = a \times C + b$, with a equal to 0.1327 d^{-1} and defined as the slope and b equal to - 0.1709 g L^{-1} d^{-1} and defined as the interception of curve r versus C. The figure shows a very good correlation between r and C; both fit a linear line with a correlation greater than 96% (R^2 = 0.9601). The substrate removal kinetics for the APBR treating the AAP-contaminated brewery wastewaters could be expressed in terms of r, and, by equating it to zero, the minimum C value of approximately 1.29 g L^{-1} can be obtained. Under unfavourable conditions, the APBR treatment process could be capable of removing oxidable organic matter from brewery wastewaters with the maximum COD concentration of 3.71 g L^{-1} (5 - 1.29 g L^{-1}) allowed in the effluent.

(**Fig. 6** could be here)

The volumetric CH_4 production rate can be calculated using the equation of $r_m = P/V$, where r_m is the volumetric CH_4 production rate (in L of CH_4 L^{-1} d^{-1}), P is the daily CH_4 production (in L of CH_4 d^{-1}) and V is the APBR volume (in L) (Borja et al., 2003). A plot (Fig. 6; see curve-2) of r_m versus C can determine a logarithmic regression model equation to represent the experimental data in the form of $r_m = c \times \ln(C) + d$, where c equals 0.3038 L of CH_4 g^{-1} d^{-1} and d equals 0.1035 L of CH_4 L^{-1} d^{-1}. The figure shows a good correlation between r_m and C, and both fit a logarithmic line with a correlation greater than 83% ($R^2 = 0.8321$). In this study, the kinetics of CH_4 production from the co-digestion of brewery wastewaters with the addition of AAP can be investigated to describe and evaluate methanogenesis. The kinetics of CH_4 production for the APBR treating the AAP-contaminated brewery wastewaters could be expressed in terms of r_m and, by equating it to zero, the minimum C value of approximately 0.3 g L^{-1} can be obtained. The APBR treatment process could be able to produce CH_4 gas from fermentable organic matter (FOM) even though its performance under unfavourable conditions would specify a maximum COD concentration of 4.7 g L^{-1} (5 - 0.3 g L^{-1}) allowed in the effluent. In accordance with the model, apparent first-order kinetics of CH_4 generation were valid for the APBR treatment process (Vavilin, 2013) due to the rate of chemical reaction effectively depending on FOM; therefore, the value of the exponent is one (Fulazzaky et al., 2013b). The value of C when r equals zero (Fig. 6; see curve-1) is higher than that when r_m equals zero (Fig. 6; see curve-2) because a high VFA concentration can be observed at the beginning of the addition of AAP to the brewery wastewaters (see Fig. 3b), yet it was converted to CH_4 and CO_2 as the end products of fermentation.

4. Conclusions

Although the APBR performance for CH_4 production remained low under unfavourable conditions for bacterial growth, the digestibility of different AAP concentrations added to brewery wastewater had a significant effect on the COD and TOC removal efficiencies. The greatest APBR performances were verified as high as 98 and 93% for the removals of COD and TOC, respectively, after the addition of AAP with the different concentrations of 5, 10 and 15 mg L^{-1}. Once the anaerobic bacteria have adapted to their environments, the decrease in percentage of CH_4 production after the injection of AAP with the concentrations of 10 and 15 mg L^{-1} in brewery wastewater could be balanced by an increased CO_2 production under steady-state conditions. The kinetics of substrate utilisation and CH_4 production can be useful for assessing digester performance. Consequently, the oxidable organic removal performance can be predicted well with the empirical kinetic model.

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References

Abdullah, N., Yuzir, A., Curtis, T.P., Yahya, A., Ujang, Z., 2013. Characterization of aerobic granular sludge treating high strength agro-based wastewater at different volumetric loadings. Bioresour. Technol., 127, 181-187.

Alidina, M., Li, D., Ouf, M., Drewes, J.E., 2014. Role of primary substrate composition and concentration on attenuation of trace organic chemicals in managed aquifer recharge systems. J. Environ. Manage., 144, 58-66.

American Public Health Association (APHA)., 2005. Standard Methods for the Examination of Water and Wastewater, 21st edn. American Public Health Association, Washington, DC.

Arcury, E.J., 1982. Continuous ethanol production and cell growth in an immobilized-cell bioreactor employing *Zymomonas mobilis*. Biotechnol. Bioeng., 24, 595-604.

Ba, S., Jones, J.P., Cabana, H., 2014. Hybrid bioreactor (HBR) of hollow fiber microfilter membrane and cross-linked laccase aggregates eliminate aromatic pharmaceuticals in wastewaters. J. Hazard. Mater., 280, 662-670.

Bah, H., Zhang, W., Wu, S., Qi, D., Kizito, S., Dong, R., 2014. Evaluation of batch anaerobic co-digestion of palm pressed fiber and cattle manure under mesophilic conditions. Waste Manage., 34, 1984-1991.

Barthakur, A., Bora, M., Singh, H.D., 1991. Kinetic model for substrate utilization and methane production in the anaerobic digestion of organic feeds. Biotechnol. Progress, 7, 369-376.

Bell, K.Y., Wells, M.J.M., Traexler, K.A., Pellegrin, M.-L., Morse, A., Bandy, J., 2011. Emerging pollutants. Water Environ. Res., 83, 1906-1984.

Borja, R., Martn, A., Rincn, B., Raposo, F., 2003. Kinetics for substrate utilization and methane production during the mesophilic anaerobic digestion of two phases olive pomace (TPOP). J. Agric. Food Chem., 51, 3390-3395.

Botz, R., Pokojski, H.-D., Schmitt, M., Thomm, M., 1996. Carbon isotope fractionation during bacterial methanogenesis by CO_2 reduction. Organic Geochem., 25, 255-262.

Chen, Z., Wang, H., Chen, Z., Rena, N., Wang, A., Shi, Y., Li, X., 2011. Performance and model of a full-scale up-flow anaerobic sludge blanket (UASB) to treat the pharmaceutical wastewater containing 6-APA and amoxicillin. J. Hazard. Mater., 185, 905-913.

Conrad, R., 1999. Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. FEMS Microbiol. Ecol. 28, 193-202.

Coskuner, G., Ballinger, S.J., Davenport, R.J., Pickering, R.L., Solera, R., Head, I..M., Curtis, T.P., 2005. Agreement between theory and measurement in quantification of ammonia-oxidizing bacteria. Appl. Environ. Microbiol., 71, 6325-6334.

Crepaldi, R.M.C., Monteiro, C., Peterlini, M.A.S., Pedreira, M.L.G., 2010. Hydrogen-ion potential of antibiotics according to the environment factors temperature and luminosity. Rev. Lat. Am. Enfermagem., 18, 278-286.

de Graaff, M.S., Vieno, N.M., Kujawa-Roeleveld, K., Zeeman, G., Temmink, H., 2011. Fate of hormones and pharmaceuticals during combined anaerobic treatment and nitrogen removal by partial nitritation-anammox in vacuum collected black water. Water Res., 45, 375-383.

dos Reis, C.M., Silva, E.L., 2014. Simultaneous coproduction of hydrogen and ethanol in anaerobic packed-bed reactors. BioMed Res. Int., 2014, 921291.

Duran, A., Monteagudo, J.M., Carnicer, A., Ruiz-Murillo, M., 2011. Photo-Fenton mineralization of synthetic municipal wastewater effluent containing acetaminophen in a pilot plant. Desalination, 270, 124-129.

Ferraz Jr, A.D., Zaiat, M., Gupta, M., Elbeshbishy, E., Hafez, H., Nakhla, G., 2014. Impact of organic loading rate on biohydrogen production in an up-flow anaerobic packed bed reactor (UAnPBR). Bioresour. Technol., 164, 371-379.

Franke-Whittle, I.H., Walter, A., Ebner, C., Insam, H., 2014. Investigation into the effect of high concentrations of volatile fatty acids in anaerobic digestion on methanogenic communities. Waste Manage., 34, 2080-2089.

Fulazzaky, M.A., 2013. Calculation of the release of total organic matter and total mineral using the hydrodynamic equations applied to palm oil mill effluent treatment by cascaded anaerobic ponds. Bioprocess Biosyst. Eng., 36, 11-21.

Fulazzaky, M.A., Abdullah, N.H., Yusoff, A.R.M., Paul, E., 2015. Conditioning the alternating aerobic-anoxic process to enhance the removal of inorganic nitrogen pollution from a municipal wastewater in France. J. Clean. Prod., 100, 195-201.

Fulazzaky, M.A., Talaiekhozani, A., Abd Majid, M.Z., Ponraj, M., Goli, A., 2013a. Evaluation of gas retention time effects on the bio-trickling filter reactor performance to treat air contaminated with formaldehyde. RSC Adv., 3, 17462-17468.

Fulazzaky, M.A., Talaiekhozani, A., Hadibarata, T., 2013b. Calculation of the optimal gas retention time using the logarithmic equation applied to bio-trickling filter reactor for formaldehyde removal from synthetic contaminated air. RSC Adv., 3, 5100-5107.

Galhetas, M., Mestre, A.S., Pinto, M.L., Gulyurtlu, I., Lopes, H., Carvalho, A.P., 2014. Carbon-based materials prepared from pine gasification residues for acetaminophen adsorption. Chem. Eng. J., 240, 344-351.

Gullicks, H., Hasan, H., Das, D., Moretti, C., Hung, Y.-T., 2011. Biofilm fixed film systems. Water, 3, 843-868.

Jefferson, B., Palmer, A., Jeffrey, P., Stuetz, R., Judd, S., 2004. Grey water characterisation and its impact on the selection and operation of technologies for urban reuse. Water Sci. Technol., 50, 157-164.

Jones, O.A., Voulvoulis, N., Lester, J.N., 2004. Potential ecological and human health risks associated with the presence of pharmaceutically active compounds in the aquatic environment. Crit. Rev. Toxicol., 34, 335-350.

Jong, T., Parry, D.L., 2003. Removal of sulfate and heavy metals bysulfate reducing bacteria in a bench scale upflow anaerobic packed bed reactor. Water Res., 37, 3379-3389.

Kim, M., Bae, W., Speece, R.E., 2004. Improved anaerobic process efficiency using mesophilic and thermophilic elutriated phased treatment. J. Environ. Eng., 130, 960-966.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones and other organic wastewater contaminants in U.S. streams, 1999-2000: a national reconnaissance. Environ. Sci. Technol., 36, 1202-1211.

Kummerer, K., 2011. Emerging contaminants. Treatise on Water Science, Vol. 3: Aquatic Chemistry and Biology. Elsevier B.V., Amsterdam, pp. 69-87.

Lin, H., Gao, W., Meng, F., Liao, B.Q., Leung, K.T., Zhao, L., Chen, J., Hong, H., 2012. Membrane bioreactors for industrial wastewater treatment: A critical review. Crit. Rev. Environ. Sci. Technol., 42, 677-740.

Málek, J., Criado, J.M., 1992. Empirical kinetic models in thermal analysis. Thermochim. Acta, 203 25-30.

Masse, D.I., Lu, D., Masse, L., Droste, R.L., 2000. Effect of antibiotics on psychrophilic anaerobic digestion of swine manure slurry in sequencing batch reactors. Bioresour. Technol., 75, 205-211.

Méndez, R., Pan, L.M., Lema, J.M.,1989. Effect of C/N/P ratio on the performance of a down-flow stationary fixed film reactor (DSFFR) working at low organic loading rates. Water Sci. Technol., 21, 1673-1676.

Mendoza, A., Aceña, J., Pérez, S., López de Alda, M., Barceló, D., Gil, A., Valcárcel, Y., 2015. Pharmaceuticals and iodinated contrast media in a hospital wastewater: A case study to analyse their presence and characterise their environmental risk and hazard. Environ. Res., 140, 225-241.

Michaud, S., Bernet, N., Buffière, P., Delgenès, J.P., 2005. Use of the methane yield to indicate the metabolic behaviour of methanogenic biofilms. Process Biochem., 40, 2751-2755.

Mostafa, M.H., Sheweita, S.A., Abdel-Moneam, N.M., 1990. Influence of some anti-inflammatory drugs on the activity of aryl hydrocarbon hydroxylase and the cytochrome P450 content. Environ. Res., 52, 77-82.

Murray, K.E., Thomas, S.M., Bodour, A.A., 2010. Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment. Environ. Pollut., 158, 3462-3471.

Nandy, T., Kaul, S.N., 2001. Anaerobic pre-treatment of herbal–based wastewater using fixed–film reactor with recourse to energy recovery. Water Res., 35, 351-362.

Narang, J., Malhotra, N., Singh, S., Singh, G., Pundir, C.S., 2015. Monitoring analgesic drug using sensing method based on nanocomposite. RSC Adv., 5, 2396-2404.

Narihiro, T. Abe, T., Yamanaka, Y., Hiraishi, A., 2004. Microbial population dynamics during fed-batch operation of commercially available garbage composters. Appl. Microbiol. Biotechnol., 65, 488-495.

Nguyen, L.N., Hai, F.I., Kang, J., Price, W.E., Nghiem, L.D., 2013. Coupling granular activated carbon adsorption with membrane bioreactor treatment for trace organic contaminant removal: Breakthrough behaviour of persistent and hydrophilic compounds. J. Environ. Manage., 119, 1773-181.

Nikolaou, A., 2013. Pharmaceuticals and related compound as emerging pollutants in water: analytical aspects. Global NEST J., 15, 1-12.

Novak, J.T., Sadler, M.E., Murthy, S.N., 2003. Mechanisms of floc destruction during anaerobic and aerobic digestion and the effect on conditioning and dewatering of biosolids. Water Res., 37, 3136-3144.

Olsson, L., Fallde, M., 2015. Waste(d) potential: a socio-technical analysis of biogas production and use in Sweden. J. Clean. Prod., 98, 107-115.

Patra, A.K., Yu, Z., 2013. Effects of coconut and fish oils on ruminal methanogenesis, fermentation, and abundance and diversity of microbial populations in vitro. J. Dairy Sci., 96, 1782-1792.

Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. Water Res., 72, 3-27.

Ramachandran, R., Saraswathy, M., 2014. Up-regulation of nuclear related factor 2 (NRF2) and antioxidant responsive elements by metformin protects hepatocytes against the acetaminophen toxicity. Toxicol. Res., 3, 350-358.

Ruiz, B., Flotats, X., 2014. Citrus essential oils and their influence on the anaerobic digestion process: An overview. Waste Manage., 34, 2063-2079.

Satya, E.J., Venkateswarlu, C., 2013. Evaluation of anaerobic biofilm reactor kinetic parameters using ant colony optimization. Environ. Eng. Sci., 30, 527-535.

Scullion, J., Winson, M., Matthews, R., 2007. Inhibition and recovery in a fixed microbial film leachate treatment system subject to shock loading of copper and zinc. Water Res., 41, 4129-4138.

Seppälä, M., Paavola, T., Lehtomäki, A., Rintala, J., 2009. Biogas production from boreal herbaceous grasses – Specific methane yield and methane yield per hectare. Bioresour. Technol., 100, 2952-2958.

Shariati, F.P., Mehrnia, M.R., Salmasi, B.M., Heran, H., Wisniewski, C., Sarrafzadeh, M.H., 2010. Membrane bioreactor for treatment of pharmaceutical wastewater containing acetaminophen. Desalination, 250, 798-800.

Singh, S.P., Prerna, P., 2009. Review of recent advances in anaerobic packed-bed biogas reactors. Renew. Sust. Energy Rev., 13, 1569-1575

Sponza, D.T., Demirden, P., 2007. Treatability of sulfamerazine in sequential upflow anaerobic sludge blanket reactor (UASB)/completely stirred tank reactor (CSTR) processes. Separ. Purif. Technol., 56, 108-117.

Stackelberg, P.E., Gibs, J., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Lippincott, R.L., 2007. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. Sci. Total Environ., 377, 255-272.

Sun, Q., Lv, M., Hu, A., Yang, X., Yu, C.-P., 2014. Seasonal variation in the occurrence and removal of pharmaceuticals and personal care products in a wastewater treatment plant in Xiamen, China. J. Hazard. Mater., 227, 69-75.

Tambosi, J.L., Yamanaka, L.Y., José, H.J., Moreira, R.F.P.M., Schröder, H.F., 2010. Recent research data on the removal of pharmaceuticals from sewage treatment plants (STP). Quím. Nova, 33, 2.

Tan, C., Gao, N., Zhou, S., Xiao, Y., Zhuang, Z., 2014. Kinetic study of acetaminophen degradation by UV-based advanced oxidation processes. Chem. Eng. J., 253, 229-236.

Vavilin, V.A., 2013. Estimating changes of isotopic fractionation based on chemical kinetics and microbial dynamics during anaerobic methane oxidation: apparent zero- and first-order kinetics at high and low initial methane concentrations. Anton Leeuw., 103, 375-83.

Wang, Y., Zhang, Y., Wang, J., Meng, L., 2009. Effects of volatile fatty acid concentrations on methane yield and methanogenic bacteria. Biomass Bioenergy, 33, 848-853.

Wong, B.-T., Show, K.-Y., Su, A., Wong, R.-j., Lee, D.-J., 2008. Effect of volatile fatty acid composition on upflow anaerobic sludge blanket (UASB) performance. Energy Fuel., 22, 108-112.

Xiao, H., Song, H., Xie, H., Huang, W., Tan, J., Wu, J., 2013. Transformation of acetaminophen using manganese dioxide-mediated oxidative processes: Reaction rates and pathways. J. Hazard. Mater., 250-251, 138-146.

Yoon, S.-D., Byun, H.-S., 2013. Molecularly imprinted polymers for selective separation of acetaminophen and aspirin by using supercritical fluid technology. Chem. Eng. J., 226, 171-180.

Yu, H., Gu, G., 1996. Biomethanation of brewery wastewater using an anaerobic upflow blanket filter, J. Clean. Prod., 4, 219-223.

Zaib, Q., Mansoor, B., Ahmad, F., 2013. Photo-regenerable multi-walled carbon nanotube membranes for the removal of pharmaceutical micropollutants from water. Environ. Sci. Process. Impacts, 15, 1582-1589.

Zenker, A., Cicero, M.R., Prestinaci, F., Bottoni, P., Carere, M., 2014. Bioaccumulation and biomagnification potential of pharmaceuticals with a focus to the aquatic environment. J. Environ. Manage., 133, 378-387.

Zhang, B., He, P.J., Lü, F., Shao, L.M., Wang, P., 2007. Extracellular enzyme activities during regulated hydrolysis of high-solid organic wastes. Water Res., 41, 4468-4478.

Zinder, S.H., Anguish, T., Cardweel, S.C., 1984. Selective inhibition by 2-bromoethanesulfonate of methanogenesis from acetate in a thermophilic anaerobic digestor. Appl. Environ. Microbiol., 47, 1343-1345.

Zuccato, E., Castiglioni, S., Fanelli, R., Reitano, G., Bagnati, R., Chiabrando, C., Pomati, F., Rossetti, C., Calamari, D., 2006. Pharmaceuticals in the environment in Italy: causes, occurrence, effects and control. Environ. Sci. Pollut. Res., 13, 15-21.

Figure captions

Figure 1 Schematic of the anaerobic packed-bed reactor

Figure 2 Variations of the UAPBR efficiency pursuant to time; where (●) is the per cent removal for COD and (○) is the per cent removal for TOC, with the averages of COD and TOC removal as high as 74 and 85%, respectively

Figure 3 Variations of: **(a)** biogas productions, with (●) representing CH_4 production, (▲) representing CO_2 production and (○) representing the production of other biogases; **(b)** the concentration of VFAs observed in the bioreactor, pursuant to time

Figure 4 Variations of pH at inlet and outlet of the bioreactor, with (●) representing pH at the inlet and (▲) representing pH at the outlet of the bioreactor

Figure 5 Variations of CH_4 production and CH_4 yield pursuant to time with (○) representing CH_4 production and (●) representing CH_4 yield

Figure 6 Curves of plotting r versus C (curve-1), with the points (●) used for fitting the linear line, and r_m versus C (curve-2), with the points (▲) used for fitting the logarithmic line

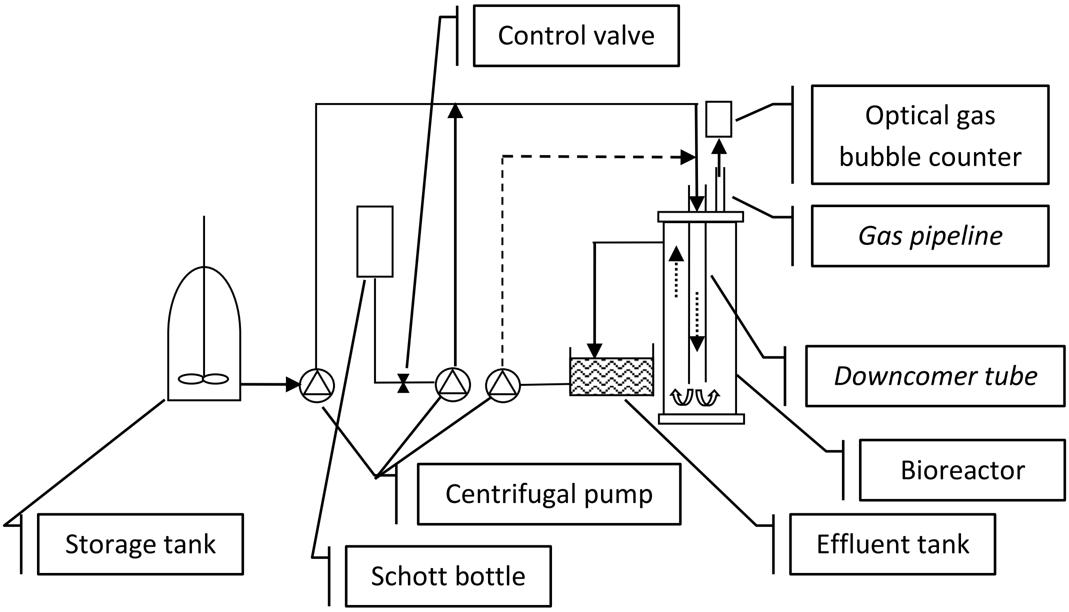


Figure 1

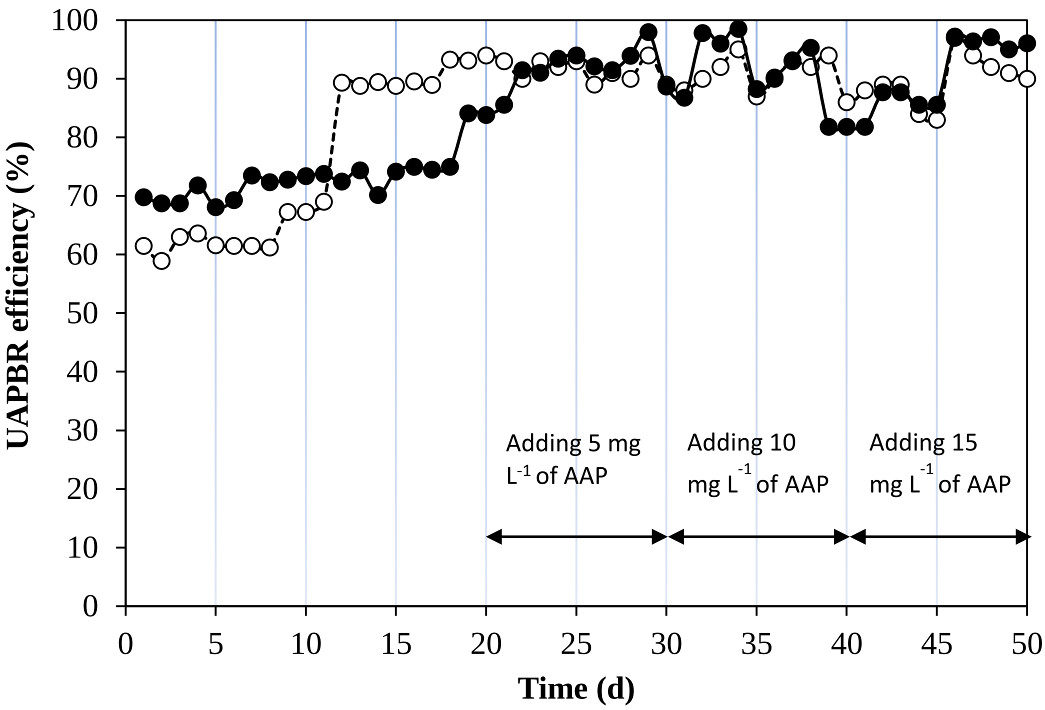
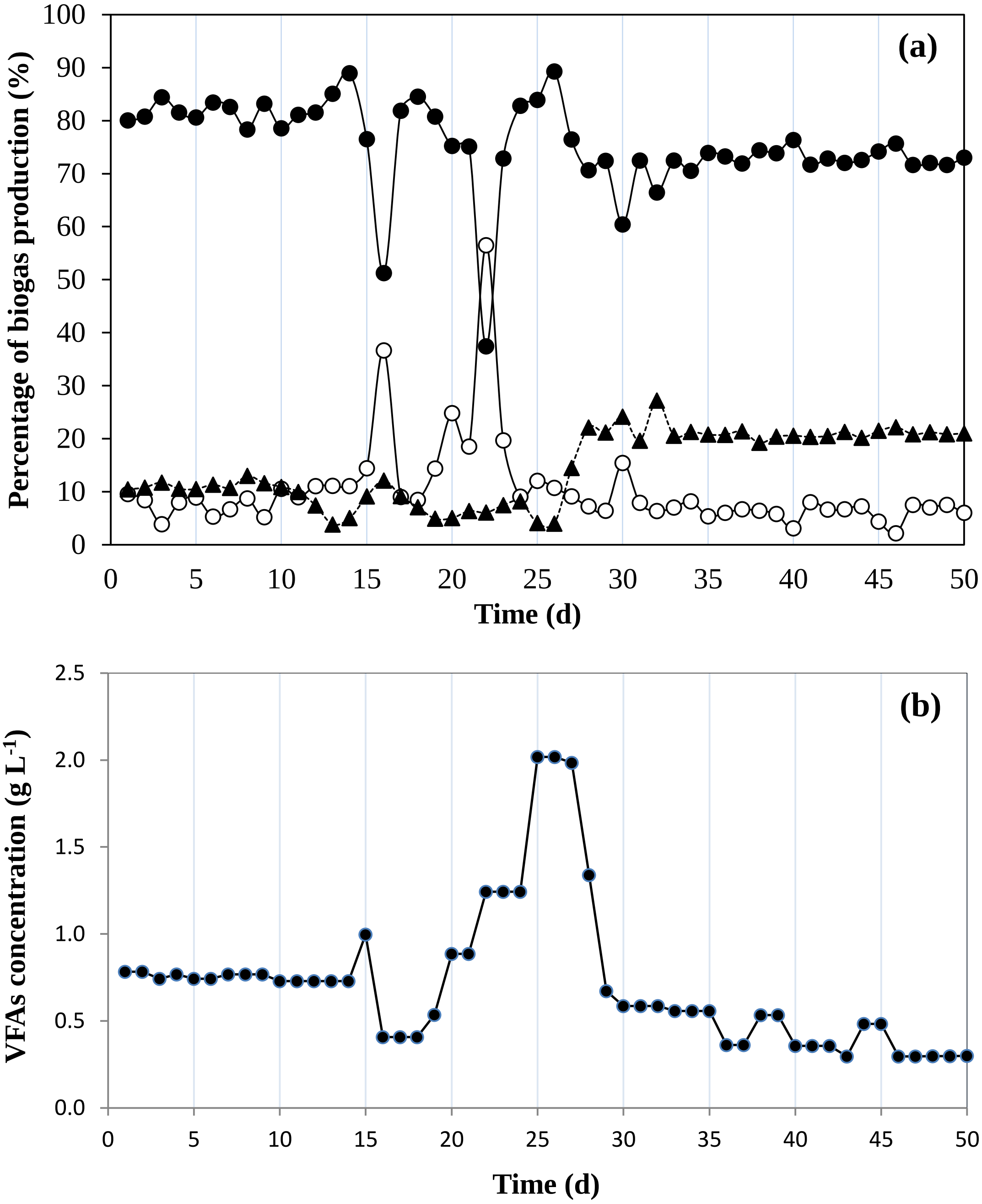


Figure 2



(a)
Percentage of biogas production (%)
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
50
Time (d)
(b)
VFAs concentration (g L-1)
2.5
2.0
1.5
1.0
0.5
0.0
0
5
10
15
20
25
30
35
40
45
50
Time (d)

Figure 3

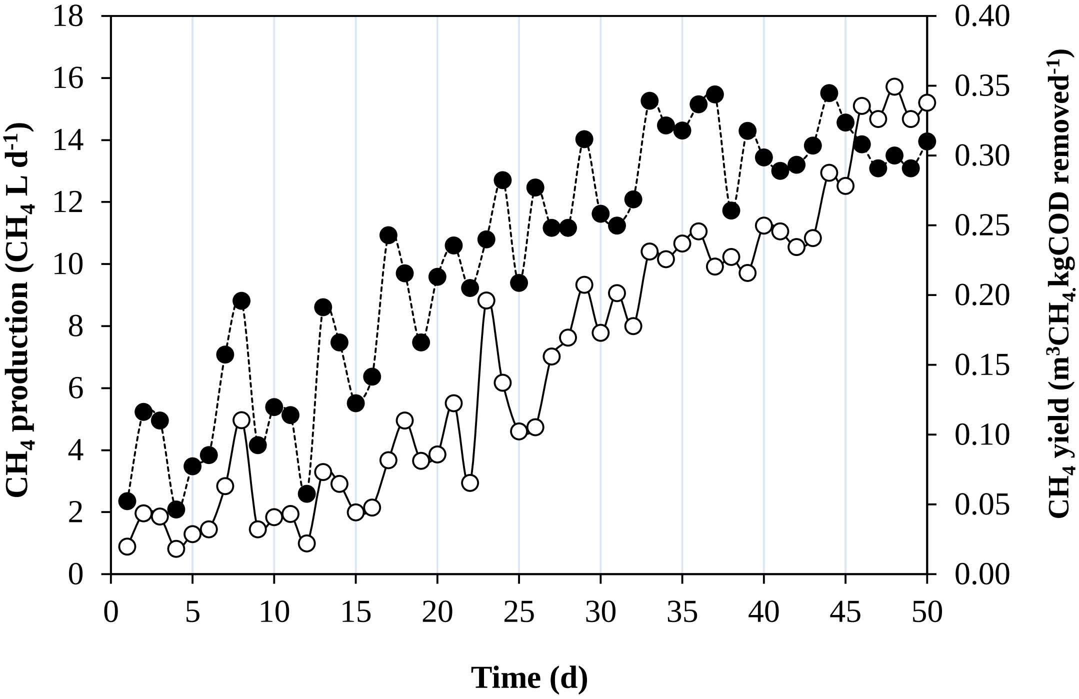


Figure 5

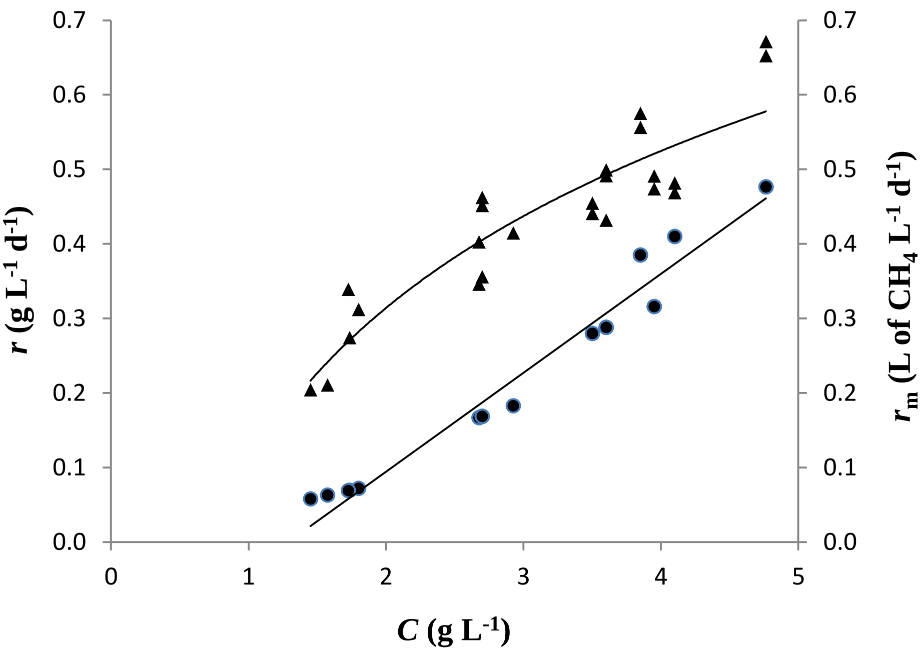


Figure 6

Table 1 Summary of the APBR operating conditions

Experimental period (d)	Duration per stage of the experiment (d)	OLR (kgCOD m^{-3} d^{-1})	Inlet COD concentration (g L^{-1})	Operating temperature (ºC)	HRT (d)	Inlet AAP concentration (mg L^{-1})
20	20	1.5	5	37	3	0
30	10	1.5	5	37	3	5
40	10	1.5	5	37	3	10
50	10	1.5	5	37	3	15